Studies on Adsorption and Wetting Phenomena Associated with Solid Surfaces in Aqueous Synthetic and Natural Surfactant Solutions

Thesis submitted by

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Under the supervision of

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Dedicated

to

My Parents

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CERTIFICATE

This is to certify that the thesis entitled ***"Studies on Adsorption and Wetting Phenomena Associated with Solid Surfaces in Aqueous Synthetic and Natural Surfactant Solutions"*** submitted by **Nihar Ranjan Biswal** (Roll No- 507CH003) to National Institute of Technology, Rourkela in partial fulfillment of the requirements for the completion of the Ph. D. degree in Chemical Engineering, is an authentic work carried out by him under my supervision and guidance.

Santanu Paria

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ABSTRACT

Adsorption of surfactants at air-liquid and solid-liquid interface and wetting of solid surfaces are closely interdependent. The performance of many physicochemical process and fundamental understanding depends on these two important phenomena. Because of the importance of these phenomena this study mainly focuses on adsorption of different surfactants at air-water and solid-water interfaces and wetting of those surfactant solutions at flat solid surfaces. The main emphasis of this study is plant-based natural surfactants; however some synthetic surfactants are also studied as a reference for comparison. The effects of electrolytes, alcohols, and natural-synthetic surfactants mixtures are also studied.

Electrolytes are most powerful inexpensive additive enhances the adsorption capacity of ionic surfactants at interfaces which in turn also enhances the interfacial behaviour. Adsorption kinetics and isotherm of anionic (dodecylbenzene sulfonate, SDBS), cationic (cetylpyridinium bromide, CPB), and non-ionic (TX-100) surfactants in the presence and absence of electrolytes on PTFE-water interface are studied. The kinetics of adsorption fits well pseudo-second-order kinetic model for the three surfactants studied here. Adsorption isotherms of TX-100 follow Langmuir type, whereas SDBS and CPB follow Freundlich type. However, in the presence of electrolytes both the ionic surfactants show better fitting with Langmuir type isotherm. The effect of electrolytes on the surfactant concentration far below the CMC shows there is a linear increase in amount adsorbed with the increase in ionic strength of the electrolyte mainly due to reduction in headgroup repulsion and finally reaches a plateau level when the equilibrium concentration reaches CMC at that electrolyte concentration.

The structure of tailgroup of non-ionic surfactants also plays an important role in both adsorption and wetting behaviour. To get some insight about the fact, the adsorption and wetting behavior of two nonionic surfactants (TX-100 and Igepal CO-630) having the same headgroup but structurally different tailgroups has been compared. The change in contact angle with the concentration of surfactant follows a trend similar to that for adsorption onto a PTFE surface. At low surfactant concentration, Igepal CO-630 shows a slightly higher adsorption density and better wetting properties than TX-100. Both surfactants show lower adsorption densities at the PTFE–water interface than at the air–water interface.

The wetting of hydrophobic and hydrophilic solid surfaces by surfactant solutions of better efficiency is an important research topic recently because of its profound practical applications. The wettability of two double-chain surfactants (cationic, didodecyldimethylammonium bromide or DDAB, and anionic, aerosol OT or AOT) solutions on PTFE and glass surfaces has been investigated here. Different physicochemical parameters such as critical micelle concentration (CMC) and surface tension, contact angle, surface excess at air–water and solid-water interfaces, work of adhesion, and free energy of wetting have been estimated for two double-chain surfactants solutions and compared with the reported results of single-chain surfactants. The double-chain surfactant solutions showed maximum lowering of surface tension values (24.36 and 26.35 mN/m for DDAB and AOT, respectively) and a change in contact angle values from pure water on PTFE (~38° for DDAB and AOT) and glass (~26.5 and 24° for DDAB and AOT, respectively) surfaces compared to the conventionally studied single-chain surfactants. The surfactant molecules mostly formed a monolayer adsorption on both surfaces during the wetting process.

The reduction in synthetic surfactant consumption in any process may lead to a significant reduction in environmental pollution. As a result, in many applications substitution of synthetic surfactants by biodegradable environmentally friendly surfactants is a latest trend. The adsorption and wetting behaviour of biodegradable, most easily and abundantly available three plant-based surfactants, Reetha, Shikakai, and Acacia on PTFE and glass surfaces have been studied here to get some idea about their efficiency compared to commonly used synthetic surfactants. The adsorption kinetics shows all the surfactants are adsorbed within 20 minutes on PTFE surface and the amount adsorbed at equilibrium of Shikakai is more in compare to Reetha and Acacia. A Langmuir-type isotherm best fits for all the surfactants. The change in contact angle on PTFE surface by the surfactant solutions also follow similar trend to that of adsorption density; the final contact values for Reetha, Acacia, and Shikakai are 109.88°, 109.02° and 98.13° respectively. The wetting studies indicate plant surfactants are inferior to the conventionally used synthetic surfactants. The adsorption studies show the density of adsorption at the PTFE-water interface is lower than the air-water interface for all three surfactants, which is also independently supported by the contact studies. The contact angle on glass surface shows that there is an increase in contact angle from 47° (pure water) to 67.72, 65.57, 68.84, and 68.79°

for Reetha Acacia, Shikakai, and Triton X-100 respectively at the saturation level with the increase in surfactant concentration.

Shikakai has shown to be better surface-active agent compared to Ritha and Acacia. To further enhance the efficiency of Shikaki effect of two different alcohols (C_1: methanol and C_5: amyl alcohol) was also studied. The addition of methanol and amyl alcohol to the Shikakai solution show there is synergistic interaction between the alcohol and Shikakai molecules and that is more for amyl alcohol. Since the interaction is more for amyl alcohol consumption of alcohol is also 1000 times lower than methanol to get similar surface tension reduction. When the concentration of Shikakai is constant with the increasing concentration of alcohols up to a certain concentration of alcohol reductions in surface tension and contact angle are more than that of pure solutions of similar concentrations because of synergistic interaction.

Further, to see efficiency of plant-synthetic mixed surfactant system, a double-chain surfactant DDAB was mixed with Shikakai. Pure Shikakai is having higher surface tension and contact angle values at CMC than that of DDAB, indicates inferior than the commonly used synthetic surfactant. Addition of DDAB on Shikakai shows there are gradual lowering of CMCs, surface tension and contact angle values at CMC. When the concentration of synthetic surfactant is ~ 50 mole % in the mixture, the final surface tension and contact angle values are close to that of pure DDAB. The mixed surfactant solutions show highly non-ideal behaviour because of interaction between two molecules which surely has some practical importance. The wetting property of Shikakai on PTFE surface increases significantly in the presence of DDAB. As the wetting property of a plant surfactant enhances in the presence of synthetic surfactant, the use of plant-synthetic mixed surfactant system may be useful in several wetting applications to reduce the surfactant based environmental pollution.

Keywords: Surfactant Adsorption, Wetting, Surface Tension, Contact Angle, Shikakai, Reetha, Acacia, DDAB, AOT, CPB, SDBS, Triton X -100, Igepal CO 630, PTFE, Glass.

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Greek symbols

α_1 = Mole fraction of Shikakai in the binary mixture

α_s = Mole fraction of surfactant

α_w = Mole fraction of water in the mixture

α_a = Mole fraction of alcohol in the mixture

β = Interaction parameter

δ = Chemical shifts (ppm)

ε_r = Dielectric constant ($C^2J^{-1}m^{-1}$)

ε_0 = Permittivity in vacuum ($C^2J^{-1}m^{-1}$)

γ, γ_{LG} = Surface tension (Liquid–Gas interfacial tension) (mN/m)

γ_{SL} = Solid–Liquid interfacial tension (mN/m)

γ_{SG} = Solid–Gas interfacial tension (mN/m)

γ_C = Critical surface tension (mN/m)

γ_L^d , γ_S^d = Dispersive forces (mN/m)

γ_L^p = Polar interaction (mN/m)

$\gamma_{w\text{-}a}$ = Surface tensions of water-alcohol mixture (mN/m)

γ_w = Surface tensions of pure water (mN/m)

γ_a = Surface tensions of pure alcohol (mN/m)

$\gamma_{a\text{-}s\ mix}$ = Surface tension values of alcohol-Shikakai surfactant mixtures (mN/m)

γ_s = Surface tension values of Shikakai surfactant (mN/m)

$\gamma_{w\text{-}a\ exp}$ = Experimental surface tension of water-alcohol mixture (mN/m)

ν_{as} = Asymmetric vibration bands (cm^{-1})

ν_s = Symmetric vibration bands (cm^{-1})

π = Pi.

θ = Contact angle (º)

Γ = Amount adsorbed at the solid-liquid interface (μMg^{-1})

Γ_{max} = Saturated surface excess concentration of the surfactant at the interface (mM/m^2)

Γ_A = Surface excess of the alcohols (mM/m^2)

Γ_S = Surface excess of the surfactant Shikakai (mM/m^2)

Γ_{SL}= Surface excess concentration of surfactant at the Solid–water interface (mM/m^2)

Γ_{SG}= Surface excess concentration of surfactant at the Solid–Air interface (mM/m^2)

Γ_{LG}= Surface excess concentration of surfactant at the Water–Air interface (mM/m^2)

κ = Debye–Huckel parameter ($Å^{-1}$)

ζ = Zeta potential (mV)

English symbols

a = A constant or coefficient of Freundlich isotherm equation

A = Hamaker constant

A_{min} = Minimum surface area occupied per molecule ($Å^2$)

b = Adsorption constant of Langmuir equation (mM^{-1})

C_e = Equilibrium concentration of surfactants in the solution (mM)

C_{eq} = Equilibrium concentrations (mM)

C_E = Concentration of surfactant (mM)

C_i = Initial and equilibrium concentrations (mM)

C_i = Molar concentration of ionic species i (mM)

C_i = Particular initial surfactant concentration from the isotherm, (mM)

D = Deviation of surface tension (%)

d = Distance between the atoms in contact (nm)

e = Elementary charge (C)

f_1, f_2 = Activity coefficients of Shikakai and DDAB respectively

ΔG_{mix} = Free energy of mixed micellization (kJ mol^{-1}),

ΔG = Wetting free energy (J/mol)

ΔH_{mix} = Enthalpy of mixed micellization (kJ mol^{-1}),

h = Initial sorption rate ($\mu Mg^{-1}min^{-1}$)

k_1 = Adsorption rate constants for pseudo–first–order (min^{-1})

k_2 = Adsorption rate constants for pseudo–second–order ($g\mu M^{-1}$ min^{-1})

k_B = Boltzmann constant (JK^{-1}).

m = Mass of the adsorbent (g)

n = A constant (reciprocal of the exponent of the Freundlich isotherm equation)

N_A = Avogadro's number ($mole^{-1}$)

q_t, = Amount of surfactant adsorbed at time t ($\mu M\ g^{-1}$)

q_e = Amount of surfactant adsorbed at equilibrium ($\mu M\ g^{-1}$)

q_m = Amount adsorbed ($\mu M\ g^{-1}$)

q_m = Amount of surfactant adsorbed on the PTFE surface, ($\mu M/g$)

R_S = % reduction of surfactant

R = Universal gas constant (8314 m^3 Pa/kg mol K)

S = Specific surface area, ($m^2 g^{-1}$)

S_{BET} = BET surface area of the PTFE powder (m^2/g)

ΔS_{mix} = Entropy of mixed micellization ($JK^{-1}\ mol^{-1}$)

t = Time

T = Absolute temperature (K)

V =Volume of surfactant solution (mL)

W_A = Work of adhesion (mJ/m^2)

x_1, x_2 = Micellar mole fraction of Shikakai and DDAB respectively

z_i = valence of ionic species i

Abbreviations

AOT = Aerosol OT

BET = Brunauer–Emmett–Teller

CMC = Critical Micellar Concentration

CPB= Cetylpyridinium bromide

CTAB = Cetyltrimethylammonium bromide

DDAB = Dimethyldioctadecylammonium bromide

IS = Ionic strength

SDBS = Sodium dodecylbenzenesulfonate

SDS = Sodium dodecyl sulfate

TX-100 = Triton X-100

Chapter 1

Introduction

1.1 Introduction.

Wetting is described by the spreading of a liquid over another solid or liquid surface. Depending on the situation, it can also be the penetration of liquid into a porous medium, displacement of one liquid by another. The contact angle, (θ) is the quantitative measurement of wettability of a liquid on a solid surface. Geometrically contact angle is defined as, the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect. The contact angle is a measure of wettability, a low contact angle means high wettability and high contact angle means poor wettability. When a liquid drop is placed on a solid surface depending on contact angle various wetting conditions are schematically presented in Figure 1.1.

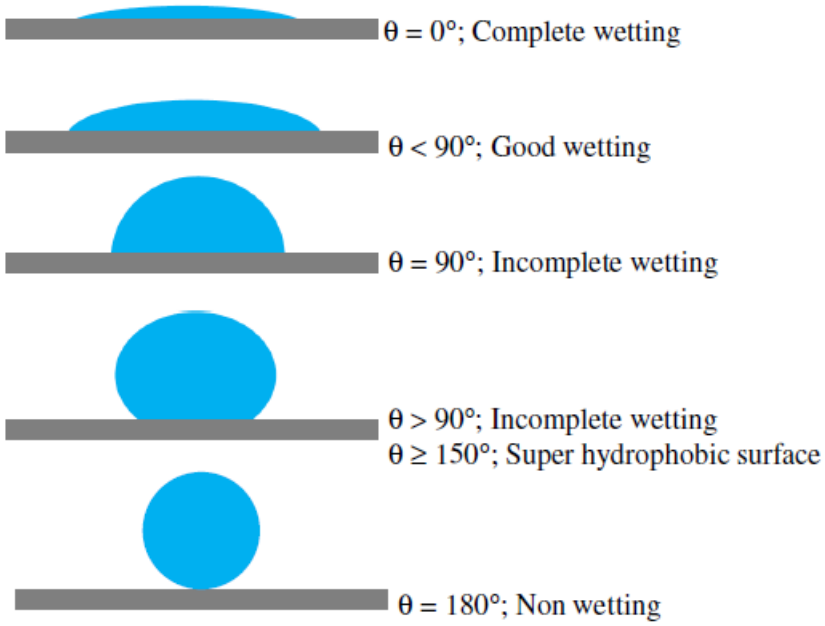


Figure 1.1 Liquid drops on a solid substrate under various wetting conditions.

The contact angle is influenced by the surface tension of the liquid, the surface free energy of the solid, and the interfacial tension which forms between the two phases.

The *wetting agents* are generally used to enhance the wettability of a liquid on solid surface; generally they are different class of surfactants or surface active agents. The role of wetting agents is to lowering of surface tension of a liquid by adsorption at air-liquid interface, at the same time they also adsorb at the solid-liquid interface. The contact angle on a solid surface can be mathematically represented from the force balance using Young's equation

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \qquad (1.1)$$

where γ_{SL}, γ_{LG}, and γ_{SG} are the interfacial tensions between the solid–liquid, air-liquid, and solid–gas interfaces respectively. Wetting can be classified into three categories: (i) spreading wetting, (ii) adhesional wetting, and (iii) immersional wetting. These processes are elaborated below.

1.1.1 Spreading Wetting

Spreading wetting a process in which a drop of liquid spreads over a solid or liquid substrate. In spreading wetting, a liquid in contact with a substrate and another fluid increases its area of contact with the substrate at the expense of the second fluid.

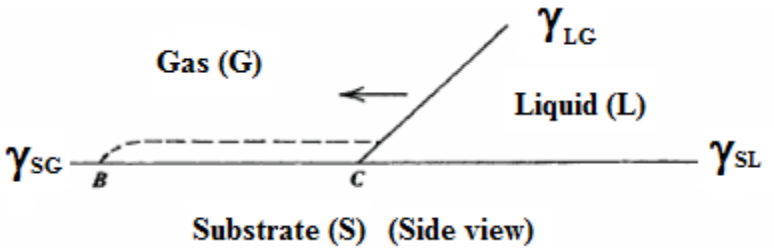


Figure 1.2 Schematics of spreading wetting (Rosen, 2004).

1.1.2 Adhesional Wetting

Adhesional wetting is a process in which an adhesional joint is formed between two phases. This quantity is known as the work of adhesion, W_A, the reversible work required to separate the unit area of liquid from the substrate. In adhesional wetting, a liquid not originally in contact with a substrate makes contact with that substrate and adheres to it.

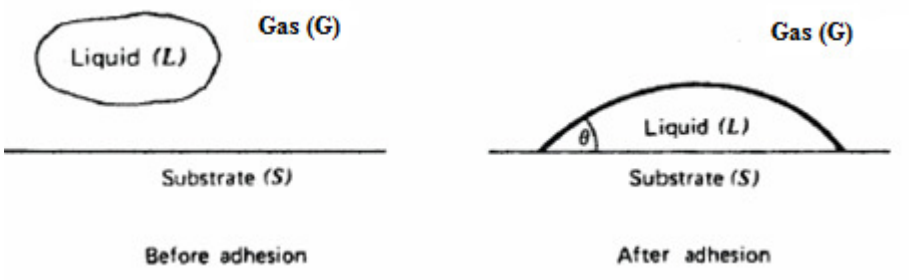


Figure 1.3 Schematics of adhesional wetting (Rosen, 2004).

1.1.3 Immersional Wetting

Immersional wetting a process in which a solid or liquid is covered with a liquid both of which were initially in contact with a gas or liquid without changing the area of the interface. In the immersional wetting, a substrate not previously in contact with a liquid is immersed completely by the liquid.

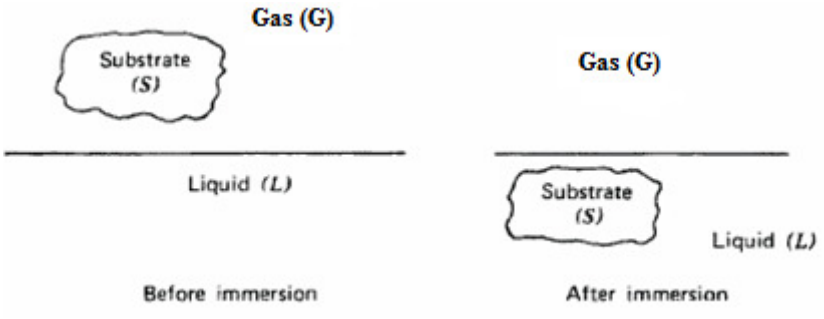


Figure 1.4 Schematics of immersional wetting (Rosen, 2004).

1.2 Importance of Adsorption in Wetting

The process of wetting of a solid by a surfactant solution is of great importance in countless applications such as oil recovery, surface cleaning, printing, painting, adhesion, lubrication, coating, flotation, dispersion and so on. In all the wetting process, adsorption of surfactants at the solid-liquid and air-water interfaces plays an important role; mostly contact angle on a solid surface by a surfactant solution depends on the adsorption density and orientation pattern of the surfactants molecules on the solid surface.

When the surface is hydrophobic (low surface energy) it is very difficult to wet by a polar solvent (high surface energy or surface tension) because of mismatch of energy between solid and liquid. In this case to enhance the wettability, surface tension reduction of solvent is essential which can be possible only by the addition of surfactants and additives, where those surfactant molecules adsorb at the interfaces to reduce the surface and interfacial tensions.

1.3 Factors Affecting Wetting

Wetting of solid by a liquid is a complex phenomenon sensitive to large number of factors which is generally affected by both the substrate and materials of spreading liquid, not only depends on surface free energy or roughness but also liquid-air surface tension as well as solid-liquid interfacial tension. There are different factors that affect wetting (Shibata et al., 2004).

1.3.1 Surface Free Energy.

During spreading process the liquid molecules are arranged on the solid surface to minimize the free energy and make the system stable. On the basis of surface energy, the solid surfaces are broadly categorized as low energy solids (hydrophobic) or high energy solids (hydrophilic) depending upon the extent to which the wetting of the surface is facilitated. As the name itself implies, hydrophilic surface means surfaces having affinity to water. Water spreads very well on these surfaces giving a contact angle less than 90°. On the other hand, on hydrophobic surfaces,

water does not spread well. The water form drops on these surfaces have higher surface energy because of higher surface area. Contact angle formed is always more than 90°.

1.3.2 Surface Roughness

Surface roughness has a significant influence on the wetting behaviour of liquids. It is evident that micro or nano level roughness on the surface provides an additional interfacial area for the spreading liquid and the true contact angle would be different than the normal contact angle. The change in contact angle or wettability because of roughness may be classified into two types: (i) petal effect and (ii) lotus effect. The term petal effect describes the fact that a water droplet on the surface of a rose petal is spherical in shape, but cannot roll off even if the petal is turned upside down. This occurs because each rose petal has a collection of micropapillae on the surface and each papillae, in turn, has many nanofolds. The red rose takes advantage of this by using a hierarchy of micro- and nanostructures on each petal to provide sufficient roughness for superhydrophobicity. This is known as the Cassie impregnating wetting regime.

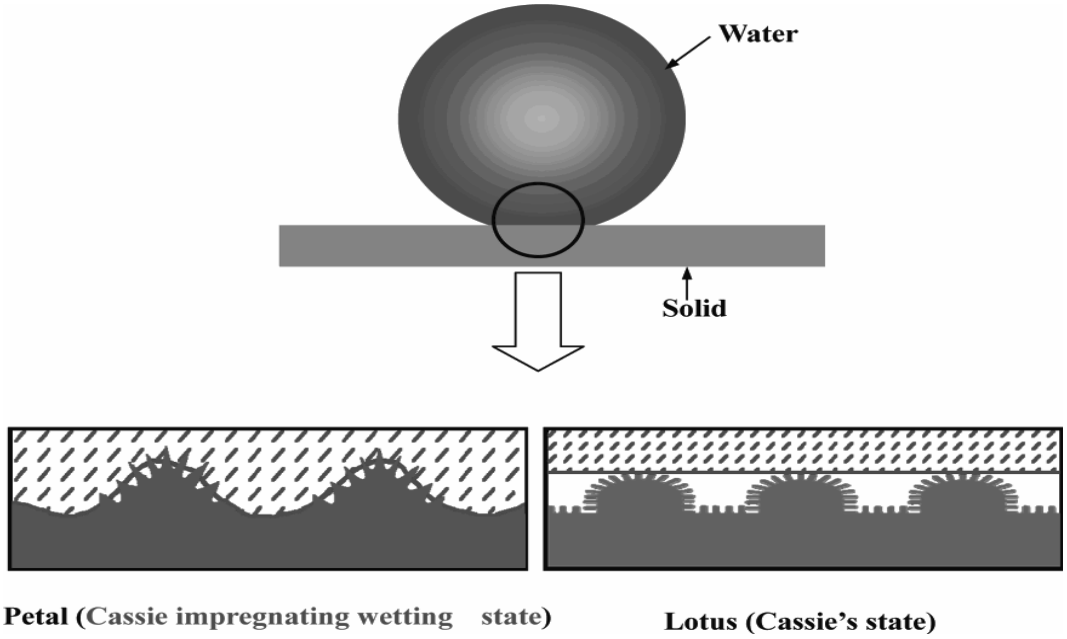


Figure 1.5 Schematic illustrations of a drop of water in contact with the petal of a red rose (the Cassie impregnating wetting state) and a lotus leaf (the Cassie's state) (Feng et al., 2008).

In case of lotus effect, the lotus leaf has a randomly rough surface and low contact angle hysteresis, which means that the water droplet is not able to wet the microstructure spaces between the spikes. This allows air to remain inside the texture, causing a heterogeneous surface composed of both air and solid. As a result, the adhesive force between the water and the solid

surface is extremely low, allowing the water to roll off easily (i.e. self-cleaning phenomena). The additional surface area provided by roughening the surface results in the increase of surface energy. The well known lotus effect of plant surfaces towards water plays a vital role in selfcleaning mechanism (Kijlstra et al., 2002; He et al., 2004).

1.3.3 Heterogeneity of the Surface

Surface cleanliness has an important influence on contact angle as any impurity present on the surface will make the surface heterogeneous (Kandlikar and Steinke, 2002). Surface heterogeneity is inevitable due to various reasons. For example, polycrystallinity, impurities present on the surface, etc. make the surface heterogeneous. Heterogeneous surfaces cause metastable equilibrium state for the system resulting in multiple contact angles. Further, a contact line traversing on a heterogeneous surface will become pinned to the patches, which generally produces lower contact angles. Surface heterogeneity also results on a very rough surface due to the entrapment of air by the liquid (Morra et al., 1990).

1.3.4 Wetting Agents.

Since water, a polar solvent has a high surface tension (72.8 mN/m), it does not spontaneously spread over solids with surface free energies smaller than 72.8 mN/m. In order to wet the surface it is essential to supplement additives like surfactants, alcohols etc. The addition of surfactants to water to modify the interfacial tension of the system is therefore often necessary to enable water to wet the surface of the solid (Rosen, 2004).

In general, nonionic surfactants are preferable in many applications because of their biocompatibility, lower sensitivity toward electrolytes, low CMC and surface tension values compare to those of ionics, and so on. In contrast to nonionics addition of ionic surfactants to aqueous solutions has much larger effect on wetting conditions. Cationic surfactants are most widely used for the wetting control, because the surfaces of the majority of inorganic natural and man-made materials are usually charged negatively. Electrostatic interaction leads to the surface hydrophobization owing to the orientation of cationic surfactant molecules by their hydrophobic groups toward the solution. In contrast to this, the adsorption of anionic surfactants from aqueous solutions increases the negative charge of hydrophilic surface and the thickness of wetting films, thus enhancing the contact angle.

Dimeric or Double-chained (e.g. Gemini or DDAB) surfactants are a relatively new class of amphiphilic molecules that are made of two hydrophobic chains and two polar headgroups

covalently attached by a spacer group or near the head groups (Cao et al., 2006). In comparison with the single-chain surfactants, dimeric surfactants have a lot of superior properties such as lower critical micelle concentrations, better wetting properties, lower limiting surface tensions, unusual aggregation morphologies, and so forth. Since dimeric surfactants have so many different properties from single-chain surfactants, the adsorption behavior of dimeric surfactants on solid surfaces has also attracted interests (Pisarcik et al., 2005).

1.3.5 Temperature

The wetting behaviour of liquid on solid is sensitive to temperature. It is a common observation that there is a decrease in viscosity and surface tension of the liquid with increase in temperature. Hence, wettability should improve for any systems with the increase in temperatures (Bernardin et al., 1997).

1.4 Contact Angle Measurement Techniques

There are two commonly used methods to measure the contact angle of a liquid on a solid surface are optical tensiometry (goniometry) and forced tensiometry. Under goniometry methods different techniques such as sessile drop or pendant drop, captive bubble, and under tensiometry methods wilhelmy balance technique have been used to study static and dynamic contact angle measurements for wettability on flat surfaces by surfactant solutions. Optical tensiometry involves the observation of a sessile drop of test liquid on a solid substrate. Force tensiometry involves measuring the forces of interaction as a solid is contacted with a test liquid. To determine the contact angle of colloids typical for soils and sediments different approaches are used as thin layer wicking and column wicking. In general each measurement techniques have some advantages and disadvantages.

They can be divided into two classes

(1) Static contact angle measurement: -a measurement at the solid/liquid interface which is not in motion.

The conventional sessile drop and captive bubble techniques are the examples.

(2) Dynamic contact angle measurement: -a measurement where the liquid front is in motion with respect to the solid surface.

1.4.1 Sessile or Pendant Drop Method

In this sessile drop method a liquid drop is to be placed on a flat smooth solid surface. The advancing contact angle was determined by placing a drop of water on the surface using a

syringe. Subsequently the drop volume is increased by adding more water to the drop. For the determination of the receding contact angle some water was drawn out of the drop causing the drop to reduce in size.

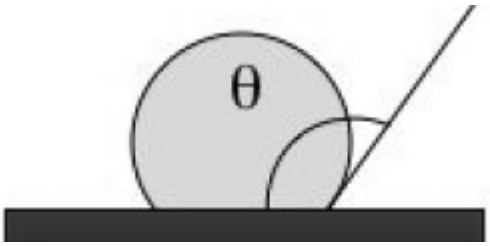


Figure 1.6 Contact angle measured by sessile or static drop method (Shang et al., 2008).

1.4.2 Captive air Bubble Method

In this method, the contact angle is measured between an air bubble of defined volume and the solid surface immersed in the temperature controlled bath.

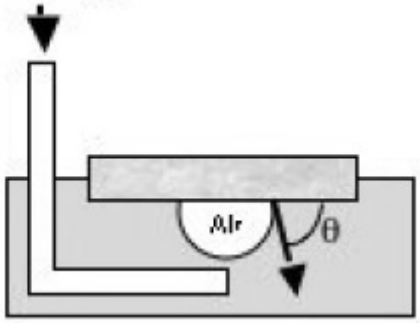


Figure 1.7 Contact angle measured by captive air bubble method (Shang et al., 2008).

1.4.3 Capillary Rise Method

The capillary rise method presents the only method of contact angle measurement available for the measurement of tubular materials and coatings.

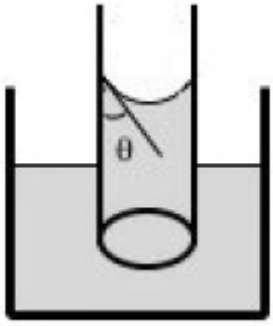


Figure 1.8 Contact angle measured by capillary rise method (Shang et al., 2008).

1.4.4 Wilhelmy Method

Force tensiometer measures the forces that are present when a sample of solid is brought into contact with a test liquid. If the forces of interaction, geometry of the solid and surface tension of the liquid are known then the contact angle can be calculated. This contact angle, which is obtained from data generated as the probe advances into the liquid, is the advancing contact angle. The sample is immersed to a set depth and the process is reversed. As the probe retreats from the liquid data collected is used to calculate the receding contact angle.

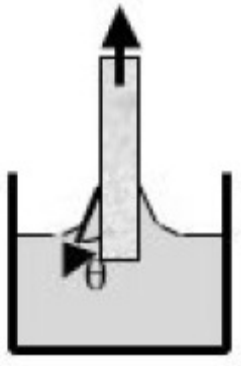


Figure 1.9 Contact angle measured by wilhelmy plate method (Shang et al., 2008).

1.5 Applications

The process of wetting of a solid by a liquid is of great technological importance for a large number of industrial as well as natural processes. Just to name a few industrial applications such as oil recovery (Fuerstenau et al., 1991), surface cleaning, printing, painting, adhesion (Neumann and Good, 1979; Adamson, 1991; Adamson and Gast, 1997; Janczuk et al., 1999; Long et al., 2005), flotation processes (Somasundaran, 1972), as agrichemical, pharmaceutical, home care products, cosmetics, and coatings (Adams, 1991; Penner et al., 1999; Gecol et al.,2001; Hill, 2002; Schramm, 2005; Tadros et al., 2005), lubrication, soldering, brazing (Schwartz and Tejada, 1972; Frear et al., 1991; Kijlstra et al., 2002; He et al., 2004), which is not at all possible to consider without wetting.

1.5.1 Enhanced Oil Recovery

Spontaneous imbibition of water into fractured reservoirs is a cheap and, therefore, important secondary oil recovery method. The technique appears to function quite well under water-wet to mixed-wet conditions. Under oil-wet/ neutral-wet conditions, however, water will not imbibe spontaneously into the matrix blocks due to a negative capillary pressure.

Wettability alteration using surfactants is related to adsorption of the surface-active chemical onto the mineral surface forming either a monolayer or a bilayer. If a monolayer is formed, the rock material is normally made more oil-wet, while the opposite happens if a bilayer is formed. Surfactant molecules in the bilayer are usually bonded to the surface through rather weak hydrophobic interactions, and they are easily removed from the surface, resulting in a completely reversible wettability alteration.

1.5.2 Detergency and Surface Cleaning

Detergency can be defined as removal of soil (particulate or oily matter) from the surface in the presence of surfactants. For the removal of particulate and oily soil contact angle plays a major role. Generally reduction of contact angle at the solid surface enhances the detergency performance.

1.5.3 Froth Flotation

When there is strong interaction between the hydrophilic groups in the surfactant and the ionic or polar sites on the substrate, adsorption of the surfactant at the solid- liquid interface occurs in such fashion that the amphipathic surfactant molecules are oriented with their polar ends toward the substrate and their hydrophobic tails toward the water. Adsorption in this manner can occur with ionic or polar substrates. Such adsorption makes the surface of the substrate more nonpolar. This phenomenon is the basis for ore flotation processes. In froth flotation processes the surface-active reagents are used to induce hydrophobicity selectively to components of the feed hence it become easy to take them out. In this particular application increase in contact angle at the mineral surface enhance flotation efficiency.

1.5.4 Agricultural Applications

Many plants leafs, fruits and stems are poorly wetted or non-wetted by pure water on aqueous solutions. However, when pesticides or micronutrients are sprayed on plant surface, better wetting is essential to spread the solutions on the plant parts for better desired action as well as to reduce the consumption.

1.5.5 Catalysis

Catalysts are used to fascinate the reactant into products in several of chemical reactions. In case of heterogeneous catalysis the enhancement of contact between two phases enhances the catalytic activity. In this regard reduction of contact angle is highly essential to enhance the performance of catalyst.

1.6 Motivation

The surfactants are drawing more and more attention now-a-days because of their wide range of applications such as detergency, flotation, preparation of nanoparticles, emulsions, pharmaceutical, food products, remediation processes and so on. Most of the surfactants used in these different applications are synthetic surfactants, manufactured by synthetic chemical route. Depending on the structure of the surfactants, mostly synthetic surfactants are not biodegradable and create environmental problem. Most widely used surfactants in detergency and other industrial applications (paints, pesticides, textile and petroleum recovery chemicals etc.) are linear alkylbenzene sulphonate (LAS) and alkyl phenol ethoxylates (APE). The breakdown products of APE are more toxic to aquatic organisms than APE alone due to shortening of the ethoxylate chains to alkyl phenol carboxylates leading ultimately to nonyl and octyl Phenols. In contrast to the synthetic surfactants bio or natural surfactants are easily biodegradable, and breakdown products are also nontoxic. So, substitution or reduction of synthetic surfactants by bio- or natural surfactants becomes a promising task recently to reduce the environmental problem. Recently many developed countries are trying experimentation on bio-surfactants for different applications; however their production in huge amount is difficult to substitute synthetic surfactants, additionally cost factor will be an important issue also. In contrast natural surfactants of plant source may be promising as well as economical. As a result, some synthetic surfactants and natural surfactants are studied here to see the adsorption and wetting behaviour at solid-water interface.

1.7 Objectives

The specific objectives of this study are:

(i) To study the adsorption kinetics and isotherm of synthetic and natural *s*urfactants on the hydrophobic PTFE surface and correlation between adsorption wetting. Also to study the effect of alcohols as an additives on interfacial behaviour and wettability of plant surfactant.

(ii) To study the structural dependency of (branch and straight chain) non-ionic surfactants on wetting the PTFE surface.

(iii) To study the wetting behaviour of a cationic (didodecyldimethyl ammonium bromide, DDAB) and an anionic (Dioctyl sodium sulfosuccinate, AOT) double-chain surfactants on PTFE and glass surfaces. Comparisons with conventionally used different single-chain

surfactants to get an idea about the reduction in consumption and enhancement in performance.

(iv) To study the wettability of three different natural *s*urfactants on PTFE and glass surfaces, the solution behavior of DDAB-natural mixed surfactant system, their efficiency in wetting to reduce surfactant consumption, and enhance the efficiency. Also to see the wetting efficiency of natural surfactants in the presence of alcohols as an additive.

1.8 Organization of the Thesis

The thesis has been organized into nine chapters. *Chapters* 1 and 2 represent introduction to the topic and relevant literature review respectively. *Chapter*-3 contains effect of electrolyte solutions on the adsorption of cetylpyridinium bromide (CPB) and sodiumdodecylbenzene sulfonate (SDBS) surfactants at the PTFE–water interface. *Chapter* - 4 presents comparison of adsorption and wetting behavior of two non-ionic surfactants (Igepal CO-630 and TX-100) having straight and branch chain tail groups respectively on the PTFE surface. *Chapter* - 5 presents comparisons of solution and the wetting behaviours of two double-chain cationic (DDAB) and anionic (AOT) surfactants; as well as similar results with that of single-chain surfactants on the PTFE and the glass surfaces. *Chapter* - 6 is on adsorption and wetting of natural surfactants on the PTFE surface. Effect of alcohol chain length on the surface tension and the wetting of the PTFE surface are also studied. *Chapter* - 7 is of similar studies of the previous chapter on the glass surface. *Chapter* -8 contains solution properties of natural-synthetic mixed surfactant solutions and wettability on the PTFE surface. Finally, *Chapter* - 9 summarises, major findings of all the chapters and suggestions for immediate further work can be done on this topic.

Chapter 2

Literature Review

Chapter 2
Literature Review

2. Wetting of Different Solid Surfaces

The extent of wetting depends on the solid surface free energies (or surface tensions) of the interfaces involved such that the total energy is minimized. For a certain type solid different liquids show different degree of wettability, this essentially depends in the surface free energy of both solid and liquid. More specifically, surfaces having surface energy less than water (72.5 mN/m) generally does not wet by water. To select the optimal conditions for wettability it is important to know not only the bulk and interfacial properties of the wetting liquids, but also the nature of the solid surfaces. The solid surfaces are broadly categorized as hydrophobic or hydrophilic depending upon the extent to which the wetting of the surface is facilitated. The name itself implies, hydrophilic surface means surfaces having affinity to water. Water spreads very well on these surfaces giving a contact angle less than 90°. On the other hand, on hydrophobic surfaces, water does not spread well. Spreading and wetting behaviour of different surfactant solutions on different surfaces have been studied by numerous researches during past few decades highlighting different aspects on this area will be discussed in the following sections. (Zisman, 1964; Stoebe et al., 1996; Stoebe et al., 1997a, b; Wagner et al., 2000; Dutschk et al., 2003a, b; Dutschk and Breitzke, 2005; Wei-Ping et al., 2009; Radulovic et al., 2009a, b).

2.1 Wetting of Hydrophobic Surfaces

Wetting of low energy or hydrophobic surfaces by polar liquids is a major challenge to the scientist because of its practical importance (Neumann and Good, 1979; Fuerstenau et al., 1991; Adamson, 1991; Adamson and Gast, 1997; Janczuk et al., 1999; Long et al., 2005; Penner et al., 1999; Gecol et al., 2001; Hill, 2002; Schramm, 2005; Tadros et al., 2005). Wetting hydrophobic surfaces are important in several applications such as oil recovery (Fuerstenau et al., 1991), surface cleaning, printing, painting, adhesion (Neumann and Good, 1979; Adamson, 1991; Adamson and Gast, 1997; Janczuk et al., 1999; Long et al., 2005), as agrichemical, pharmaceutical, home care products, cosmetics, and coatings (Penner et al., 1999; Gecol et al., 2001; Hill, 2002; Schramm, 2005; Tadros et al., 2005). In general, reductions of surface tension as well as solid-liquid interfacial tension enhance the wettability of hydrophobic surfaces by

polar liquids. As a result, adsorption behaviors of surfactant molecules at solid-liquid and air-liquid interfaces are most important in this process.

2.1.1. Wetting of Hydrophobic Surfaces by Single Chain Surfactant System

It has been already mentioned that the wetting hydrophobic solid surfaces depends on surface tension reduction as well as reduction of solid-liquid interfacial tension, which in turn depends on the type and structure of the surfactants. Various industrial wetting processes call for aqueous solutions to spread on difficult-to-wet surfaces. One example from the agrochemical industry is the application of pesticides to plant leaves, which are difficult-to-wet due to their waxy coating. When these solutions are applied, instead of spreading on the leaf as desired, they tend to form beads which subsequently roll off of the leaf. This limitation is overcome by the addition of surface-active agents or surfactants to the solution which reduce the interfacial tensions and increase the wetted area (Knoche, 1994). Surfactants are also used to enhance wetting in the printing, cosmetics, and painting industries. Surfactants enhance the wetting of aqueous solutions on difficult- to-wet surfaces by adsorbing at the liquid–vapor and solid–liquid interfaces. This leads to a reduction in the interfacial tension of each interface.

In the wetting process, adsorption of surfactant at the solid–liquid interface and at the air–liquid interface plays an important role. Surfactants having low critical micellar concentration (CMC) and low surface tension values at the CMC are always beneficial for the wetting process. A situation in which the addition ;of a surface-active agent to water decreases its wetting power is when adsorption of the surfactant at the solid- liquid interface occurs in such fashion that the amphipathic surfactant molecules are oriented with their polar ends toward the substrate and their hydrophobic tails toward the water. Adsorption in this manner can occur with ionic or polar substrates when there is strong interaction between the hydrophilic groups in the surfactant and the ionic or polar sites on the substrate. Such adsorption makes the surface of the substrate more nonpolar. Cationic surfactants are adsorbed in this manner onto negatively charged solid surfaces, such as quartz, cellulose textile fibers, or glass, and render them more difficult to wet with aqueous solutions than they were originally and more easily wet by nonpolar materials. This phenomenon is the basis for ore flotation processes (Somasundaran, 1972). The single chain surfactants are again can be broadly classified into anionic, cationic, non-ionic, and zwitterionic.

2.1.1.1 Wetting of Hydrophobic Surfaces by Nonionic Surfactant Solutions

In general, nonionic surfactants are preferable in many applications because of their biocompatibility, lower sensitivity toward electrolytes, low CMC and surface tension values compare to those of ionics, and so on. There are some of the studies documented on wetting of different surfaces by different nonionic surfactant solutions (Norling and Brukl, 1986; Scales et al., 1986; Gau and Zografi, 1990; Bahr et al., 2001; Musselman and Chander, 2002; Graca et al., 2007; Hunter et al., 2009; Halverson et al., 2009) anionic surfactant solutions (Zdziennicka et al., 2003; Mohammadi et al., 2004) cationic surfactant solutions (Harkot and Janczuk, 2009).

The wettability of polyy(vinyl siloxane) impression materials modified by the incorporation of members of a homologous series of nonylphenoxypoly(ethyleneoxy)ethanols surfactants of substantially different chemistries of varying HLB values has been studied by Norling and Brukl, (1986). The lowest homolog yielded contact angles which were higher than those for the unmodified control. The highest molecular weight homolog yielded contact angles which were significantly lower than those of the control. The minimum contact angle occurred for elastomers modified with an intermediate homolog. Similarly hydrophobic (siloxanated and silanated α-quartz) plates has been prepared by reaction of the base solid with trimethylchlorosilane to produce grafted trimethylsilyl groups at the particle surfaces and with thionyl chloride followed by butyl lithium to produce grafted butyl groups at the particle surfaces and these solids designated as m-SiO_2, and b-SiO_2, respectively by Scales et al. (1986). The subsequent change in contact angle of such surfaces exposed to nonionic (ethoxylated nonyl phenol and ethoxylated dodecyl ether type) surfactants has been determined over a four decade range of concentrations of 0.01 to 100 times the critical micelle concentration (CMC) for the surfactant series with a varies in range of wetting angles from 0 to 90º.

The comparison of contact angles for aqueous solutions of the nonionic surfactants, penta(oxyethylene) dodecyl monoether, $C_{12}E_5$, and penta(oxyethylene) decyl monoether, $C_{10}E_5$ on paraffin, polystyrene, and poly(methyl methacrylate) at the same surface tension has been studied by Gau and Zografi (1990). The study reveals wetting effectiveness, in terms of adhesion tension, $\gamma_{LV} \cos \theta$, or critical surface tension and found that for paraffin equal amount of adsorption at both the vapor-liquid and solid-liquid interfaces over the entire range of surface tension below the CMC. For the semi-polar solids, polystyrene and poly(methyl methacrylate) adsorption at solid-liquid interfaces is less than vapor-liquid.

The spreading of water and aqueous solutions of ethanol and nonionic surfactant on hydrophobic substrates (alkylsilane treated glass) has been investigated by Bahr et al. (2001). For the low viscous liquids and solutions, the spreading on the surface of hydrophobic glass rod was also studied and compared to the drop spreading experiment. The results for the aqueous systems show a rapid initial spreading process that abruptly halts after less than 30 ms, as the interfacial tension forces are balanced. In the case of surfactants solutions, this is followed by slower adsorption driven drift towards equilibrium conditions. The wetting and adsorption of acetylenic diol based surfactants (Surfynol® series TMDD 0-30), which are the derivatives of 2,4,7,9-tetramethyl-5-decyne-4,7-diol on hydrophobic surface, lampblack (pyrolytic graphite) and a complex pigment phthalocyanine blue that consists of hydrophobic and hydrophilic sites were studied to determine the mechanisms of wetting of heterogeneous surfaces (Musselman and Chander, 2002). The effect of the degree of ethoxylation of these surfactants on adsorption and wetting of pigments was also determined. The more hydrophobic reagents tend to show a larger initial increase in contact angle at low concentrations. As the concentration of the surfactant is increased further, contact angle decreases. Surfactants of zero ethylene oxide group (TMDD-0) and 3.5 ethylene oxide group (TMDD-3.5) show sharp decreases in contact angle (and accordingly sharp increases in the cosine of the angle) as the solubility limit of these surfactants is approached. The wetting power generally increases with ethoxylation. TMDD-20 and TMDD-30 show smaller contact angles at low concentrations than the less ethoxylated reagents. As concentration is increased, contact angle decreases less rapidly for these reagents. Such a phenomenon was also observed for the higher ethoxylated alkylphenol reagents (Tergitol NP-15). TMDD-3.5 and TMDD-10 show superior wetting at concentrations above 1 mmole l−1. TMDD-10 exhibits good wetting ability over the entire range of concentrations studied. The cosine of the advancing angles for the alkyl phenol surfactants on the pyrolytic graphite surface indicates that Triton X-100 and Tergitol NP-9 possess similar wetting capabilities over the range of concentrations studied.

The nanotribological responses of a series of nonionic polyoxyethylene surfactants (Tween 20, Tween 40, Tween 60, and Tween 80) were investigated after they were adsorbed from aqueous solution onto atomically smooth hydrophobic substrates of surfaces composed of a condensed monolayer of octadecyltriethoxysilane (OTE; contact angle $\theta > 110^{o}$) by Graca et al.

(2007). They found that the contact angle decreases with increasing surfactant concentration which is shown in figure 2.1(a) and (b).

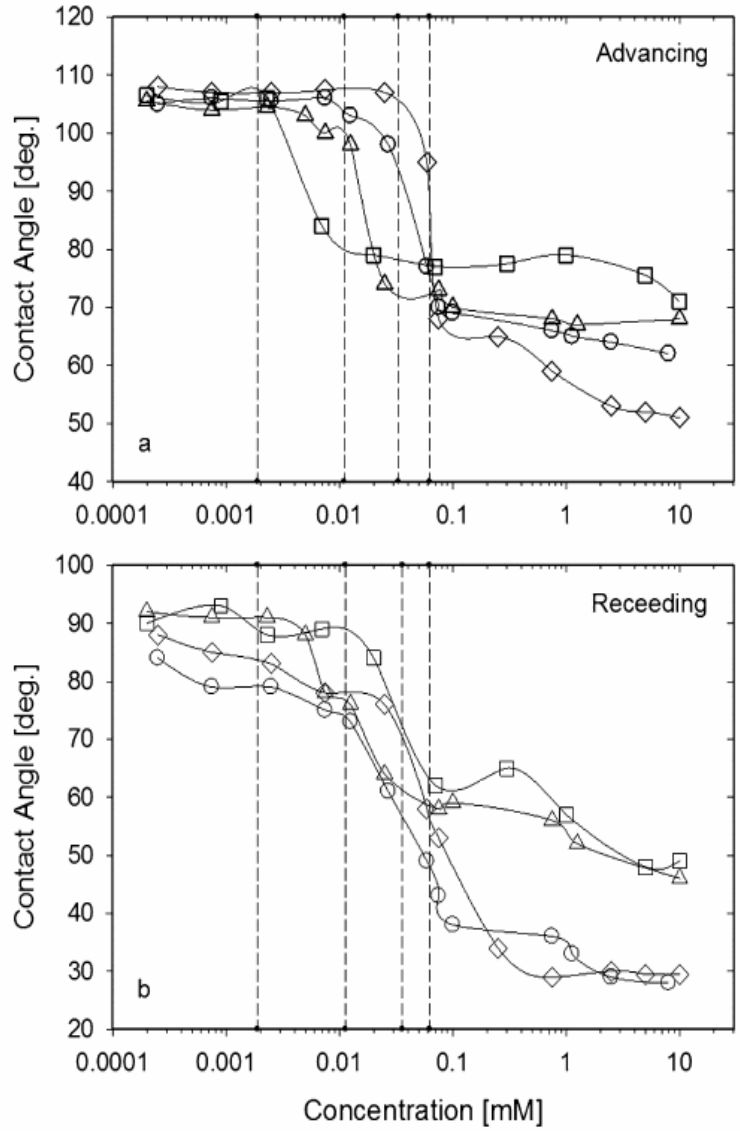


Figure 2.1(a) Advancing contact angle and (b) receding contact angle are plotted against logarithmic solution concentration for the Tween surfactants of Tween 60 (squares), Tween 80 (triangles), Tween 40 (circles), and Tween 20 (diamonds). Dashed vertical lines indicate literature values of the cmc (critical micelle concentration) of each surfactant. From left to right, the dashed lines refer to the literature cmc of Tween 60 (squares), Tween 80 (triangles), Tween 40 (circles), and Tween 20 (diamonds) (Graca et al., 2007).

The interactive behavior of octyl grafted silica particles and Triton X-100 surfactant at an air–water interface with particular reference to the effect of the interactions on the stability of

air–water foams has been investigated by Hunter et al. (2009). For a system they considered, the effects of both individual particles and surfactants with the interface, along with particle–surfactant interactions. The resulting contact angle changes for captive bubbles measured beneath the esterified silicon wafers, with increasing surfactant concentration, indicated that behavior is monotonic, with the wafers showing continued decreasing contact angle as surfactant is added into the system. This behavior was expected, as it is assumed that the surfactant adsorbs via its hydrophobic tail to the covalently bonded octyl chains, leaving the hydrophilic headgroup exposed to the liquid. Yet, if such behavior is paralleled in particle systems (as supposed), addition of surfactant may lead to a depression of the particles ability to stabilise foam systems.

Wetting of hydrophobic substrates by nanodroplets of aqueous trisiloxane and alkyl polyethoxylate surfactant solutions were carried out by Halverson et al. (2009). Trisiloxane surfactants at low concentrations promote the complete and rapid wetting of aqueous droplets on very hydrophobic (hydrocarbon) substrates. This behavior has not been demonstrated by any other surfactant which explains why the trisiloxanes are referred to as superspreaders. Here they have been conducted molecular dynamics simulations using all-atom force fields, elucidate the mechanism of superspreading.

2.1.1.2 Wetting of Hydrophobic Surfaces by Anionic Surfactant Solutions

The adsorption of anionic surfactants from aqueous solutions increases the negative charge of hydrophilic surface and the thickness of wetting films, thus enhancing the contact angle. The effect of surfactants solutions of sodium acetate, sodium dodecyl sulfate, hexadecyltrimethylammonium bromide, and *n*-decanoyl-*n*-methylglucamine on wetting behavior of super-hydrophobic surfaces, prepared of alkylketene dimer (AKD) by casting the AKD melt in a specially designed mold was investigated by Mohammadi et al. (2004). Both advancing and receding contact angles of water on the AKD surfaces increase over time (~3 days) and reach the values of about 164 and 147°, respectively. The increase of contact angles is due to the development of a prickly structure on the surface (verified by scanning electron microscopy), which is responsible for its super hydrophobicity. The contact angle results were compared to those of a number of pure liquids with surface tensions similar to those of surfactant solutions. It was found that although the surface tensions of pure liquids and surfactant solutions at high concentrations are similar, the contact angles are very different.

2.1.1.3 Wetting of Hydrophobic Surfaces by Cationic Surfactant Solutions

Addition of ionic surfactants to aqueous solutions has much larger effect on wetting conditions. Cationic surfactants are most widely used for the wetting control, because the surfaces of the majority of inorganic natural and man-made materials are usually charged negatively. Electrostatic interaction leads to the surface hydrophobization owing to the orientation of cationic surfactant molecules by their hydrophobic groups toward the solution. The adsorption of a surface-active agent at solid-water and air - water interfaces leads to changes in the interfacial tension and contact angle in a solid-liquid-air system, with wettability being a measure of solids. Since specific surfactant cannot change the interfacial tensions to such a value which will empower complete wetting, therefore, surfactants and alcohols or mixtures of surfactants are often used for greater efficiency than individual.

The role of adsorption of dodecylethyldimethylammonium bromide (C_{12}(EDMAB)) and benzyldimethyldodecylammonium bromide (BDDAB) at water–air and polytetrafluoroethylene (PTFE)–water and poly(methyl methacrylate) (PMMA)-water interface, in wetting of PTFE and PMMA surface, was established from the measured values of the contact angle (θ) of aqueous C_{12}(EDMAB) and BDDAB solutions in PTFE (PMMA)-solution drop-air system, and from the measured values of the surface tension of aqueous C_{12}(EDMAB) and BDDAB solutions by Harkot and Janczuk, (2009) and the results are presented in figure 2.2 (a) and (b).

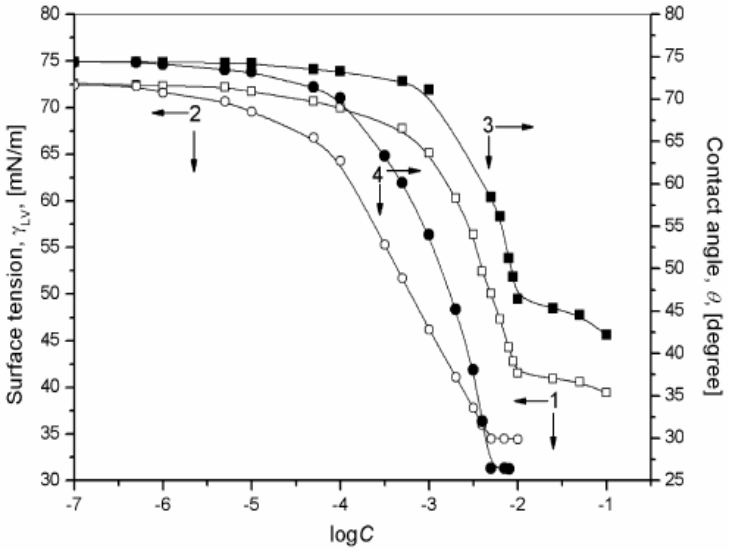


Figure 2.2(a). The relationship between the values of the surface tension (γ_{LV}) of aqueous C_{12}(EDMAB) (□) and BDDAB (○) solutions and the values of the contact angle (θ) of aqueous

C_{12}(EDMAB) (■) and BDDAB (●) solutions for the PMMA surface and the concentration of the surfactants (log C) (Harkot and Janczuk, 2009).

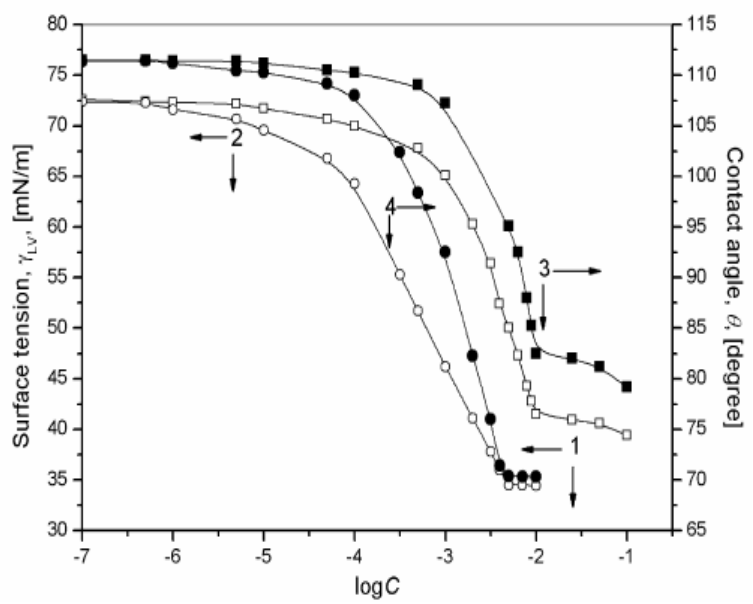


Figure 2.2(b). The relationship between the values of the surface tension (γ_{LV}) of aqueous C_{12}(EDMAB) (□) and BDDAB (○) solutions and the values of the contact angle (θ) of aqueous C_{12}(EDMAB) (■) and BDDAB (●) solutions for the PTFE surface and the concentration of the surfactants (log C) (Harkot and Janczuk, 2009).

The obtained results of the contact angle measurements indicated that the wettability of PTFE and PMMA surfaces increased with concentration increase of the surfactants, however, a complete spreading of the aqueous C_{12}(EDMAB) and BDDAB solutions over the PTFE and PMMA surfaces did not take place at any of their concentrations. Moreover, for the same BDDAB concentration in solution there were smaller values of the contact angle both on the PMMA and PTFE surface.

2.1.1.4 Wetting by Double-Chain Surfactants

Dimeric or Double-chained (e.g. Gemini or DDAB) surfactants are a relatively new class of amphiphilic molecules that are made of two hydrophobic chains and two polar headgroups covalently attached by a spacer group or near the head groups. In comparison with the single-chain surfactants, dimeric surfactants have a lot of superior properties such as lower critical micelle concentrations, better wetting properties, lower limiting surface tensions, unusual aggregation morphologies, and so forth. Since dimeric surfactants have so many different

properties from single-chain surfactants, the adsorption behavior of dimeric surfactants on solid surfaces has also attracted interests (Pisarcik et al., 2005).

There are some studies documented on wetting behaviour of different cationic gemini surfactants with varying spacer (Pisarcik et al., 2005), different head group of anionic gemin surfactants and its comparison with the monomers (Ao et al., 2009) and anionic double chain surfactants (Harkot and Janczuk, 2007).

Pisarcik et al. (2005) have studied contact angle of cationic gemini surfactant with different spacer 2, 4, and 6 in order to determined area per molecule at hydrophobic solid–water interface and found that the surfactant molecules present at the liquid/hydrophobic solid interface are almost three times as closely packed as those at the liquid/air interface. Similar expression also observed when comparison of imidazolium gemini surfactant [C_{12}-$_4$-C_{12}im]Br_2 on silicon wafer was done with its monomer [C_{12}mim]Br by Ao et al. (2009) which is shown in figure 2.3.

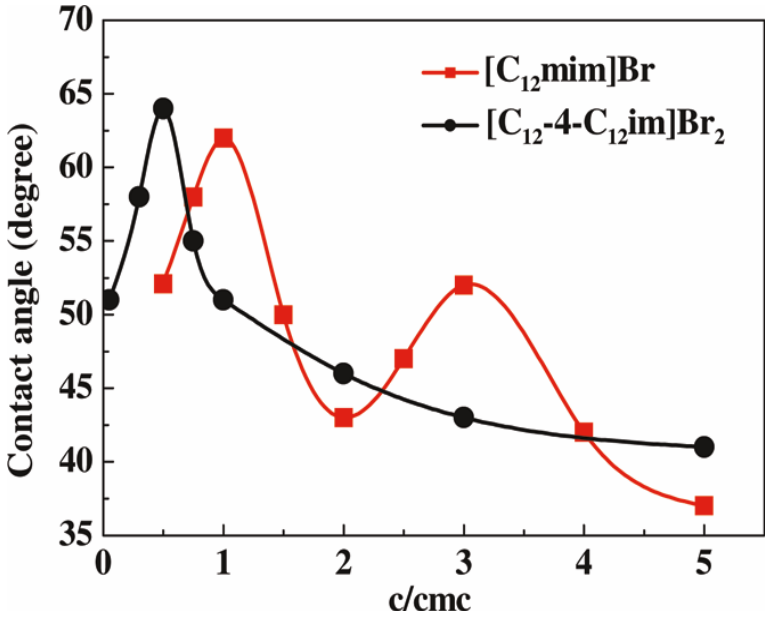


Figure 2.3 Static contact angles of silica substrates treated with [C_{12}-4-C_{12}im]Br_2 and [C_{12}mim]Br solutions at different concentrations (Ao et al., 2009).

Below the critical surface aggregation concentrations (CSAC), both surfactant molecules are adsorbed with their hydrophobic tails facing the air. But above the CSAC, [C_{12}-4-C_{12}im]Br_2 molecules finally form a bilayer structure with hydrophilic head groups facing the air, whereas [C_{12}mim]Br molecules form a multilayer structure, and with increasing its concentration. The

layer numbers increase with the hydrophobic chains and hydrophilic head groups facing the air by turns.

There also a study related to the wettability of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) on PTFE surface (Harkot and Janczuk, 2007) and found there exist a linear relation between adhesional tension versus surface tension.

2.1.1.5 Wetting by Bio-surfactants

There are some studies available on the wetting properties of different type of bio-surfactants, their salts and their comparison with the synthetic anionic surfactants (Ozdemira and Malayoglu, 2004; Ishigami et al., 1993).

To study the wetting properties of biologically produced rhamnolipids (R_L), advancing contact angles of the aqueous solutions of the R_L mixture of R_1 and R_2 in a ratio of $R_2/R_1 = 1.1$ were measured as a function of surfactant concentration by Ozdemira and Malayoglu (2004). For a comparison of the wetting performance, sodium dodecyl sulfate (SDS) was chosen as the reference surfactant. A hydrophobic polymer, polyethylene terephthalate (PET), was used as the solid surfaces to determine the wetting characteristics of rhamnolipids and results are shown in figure 2.4.

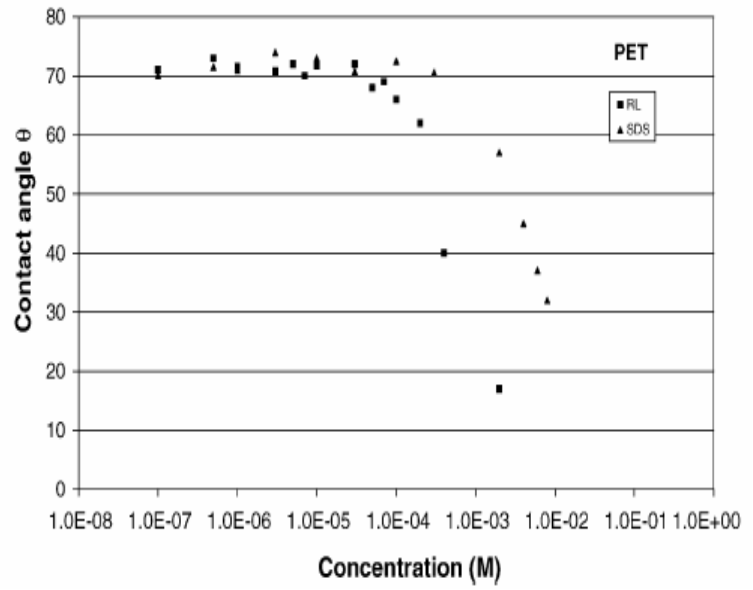


Figure 2.4 Contact angles of *R*2/*R*1 = 1.1 and SDS solutions on the PET surfaces as a function of bulk concentration (Ozdemira and Malayoglu, 2004).

At low surfactant concentrations (R_L concentration $<3 \times 10^{-5}$ M, SDS concentration $<3 \times 10^{-4}$ M) contact angle (θ) varied in a certain range depending on the character of the surfactant

interactions with the surface. This was followed by a decrease in contact angle. Parallel to this behavior, at low surfactant concentrations the adhesion tension decreased, then remained constant and an increase at higher surfactant concentrations was obtained on hydrophobic surfaces.

Ishigami et al. (1993) studied the wetting characteristics of rhamnolipids R–B–Na (sodium salt of rhamnolipid B) and its derivative R–B–Me (rhamnolipid B methyl ester) on five different kinds of polymer surfaces. Their intention was to determine the wetting properties of R–B molecules on hydrocarbon degrading microorganisms, whose surfaces are lipophilic in nature. To eliminate uncertainties in experiments they studied the wetting with polymer surfaces instead of intact living cells. They presented the measured contact angles as a function of increasing critical surface tension (γ_C) of polymer surfaces at two different R–B–Na and R–B–Me concentrations as shown in figure 2.5.

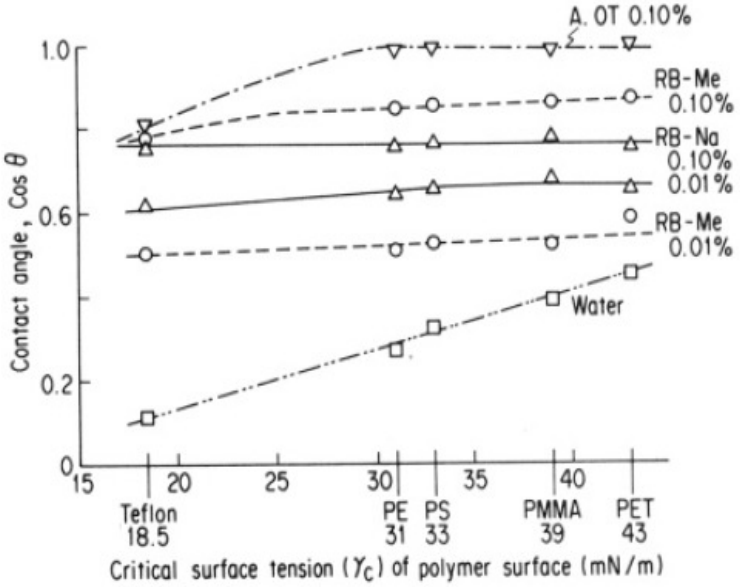


Figure 2.5 Wetting action of rhamnolipid homologues for five kinds of polymer surfaces having different y_c values (Ishigami et al., 1993).

They found that for the polymer surfaces with γc between 18.5 (PTFE) and 43 (PET) the contact angles remained almost constant at each R–B concentration, increasing only with the increase in R–B concentration. R–B molecules have three hydrophobic tails and they are more volumable molecules than R_1 and R_2.

2.1.2. Effect of Additives on Wetting Behavior of Surfactant Solutions

2.1.2.1. Effect of Alcohols on Wetting Behavior of Surfactant Solutions

Surfactants are mostly applied in the presence of additives which improve their ability to modify the interfacial properties even at low bulk concentrations. Among a very large number of additives, alcohols hold a special place because they are the most common co-surfactants which addition to surfactants strongly influences the density and structure of mixed films at different interfaces by changing their properties. In the literature there are many studies dealing with the influence of alcohol on surfactant adsorption at water–air interface. There are some studies documented on the adsorption behavior of different alcohols at air–water as well as solid–water interfaces resulting changes in wetting ability of different solid surfaces in presence of different anionic (Zdziennicka et al., 2004; Zdziennicka et al., 2005), cationic (Zdziennicka and Janczuk, 2008), and nonionic (Zdziennicka, 2009a, b; Zdziennicka, 2010a, b) surfactant solution.

The adsorption of sodium dodecyl sulphate (SDS) and propanol mixtures at air – water as well as PTFE – water interface has been studied by Zdziennicka et al. (2004). It was also found that the changes of the surface tension of the aqueous solution of SDS and propanol mixtures and PTFE-solution interface tension as a function of SDS and propanol concentration result especially from decreased contribution of the polar intermolecular interactions in the surface and interface tensions. The analysis of the excess of SDS and propanol concentration at PTFE–water interface based on results of the surface tension and contact angle measurements suggests that this excess is not a linear function of the mixture composition and that polar interactions can probably take place at the interface of PTFE-aqueous solution of the surfactant and propanol mixture. Zdziennicka et al. (2005) have examined the wettability propanol and Sodium dodecyl sulfate surfactant mixtures at constant dodecyl sulfate concentrations equal to 1×10^{-5}, 6×10^{-4}, 1×10^{-3}, and 1×10^{-2} M, respectively. Form the result it was clears that for all the four solution series of SDS and propanol mixtures at a constant SDS concentration except 1×10^{-3} M concentration though contact angle, θ value values considerably decreases with increase in propanol concentration from 0 to about 2.5M but SDS concentration has only a small influence on the contact angle values. However, in the range of propanol concentrations from 2.5 to 6.7 M the shapes of curves are similar.

Zdziennicka and Janczuk (2008) have measured the contact angles (θ) of aqueous solutions of cetyltrimethylammonium bromide (CTAB) and propanol mixtures at constant CTAB

concentration equal to 1 x 10^{-5}, 1 x 10^{-4}, 6 x 10^{-4} and 1 x 10^{-3} M on polytetrafluoroethylene (PTFE). It was observed that for each series of solutions of fixed CTAB concentration the contact angle decreased with increasing propanol concentration. However, the changes of contact angle, θ vs concentration of propanol in the range of propanol concentration from 0 to 3.21 are bigger than from 3.21 to 6.67 M. At a given low concentration of propanol contact angle decrease with increasing CTAB concentration is observed. The wetting ability of the aqueous solutions of Triton X-100 and long chain alcohol (propanol) mixtures at constant Triton X-100 concentration and short chain alcohol (methanol and ethanol) mixture at constant Triton X-100 concentration on polytetrafluoroethylene (PTFE) and polymethyhmethacrylate (PMMA) have been studied by Zdziennicka, (2009a, b) The result shows that wettability both of PTFE and PMMA by aqueous solutions of Triton X-100 and propanol mixtures depends on the propanol concentration and increases with its concentration increase. The biggest changes of PTFE wettability by the studied solutions at a given constant Triton X-100 concentration are observed in the propanol concentration, (C) range from 0.07 to 3.21 M in which propanol molecules are present rather in the monomeric than aggregated forms. In the case of PMMA a different shape of θ vs C curves is observed in comparison to PTFE. For all the series of constant concentration of Triton X-100 nearly a linear relationship occurs between θ vs C in the propanol concentration range from 0 to 4.28 M. one interesting observation obtained that for all studied solutions at C = 5.35 M, the θ = 0, so PMMA is completely wet.

On the study of the adsorption and wetting of the TX-100 and short chain alcohol (methanol and ethanol) mixtures, the surface excess at solution – air and PTFE – solution interfaces is the same, and their adsorption at solution – air is considerably higher than at PMMA–solution interface (Zdziennicka, 2009b).

Wetting of polymers (PTFE, PMMA) by aqueous solutions of Triton X-165 mixtures with methanol, ethanol and propanol was studied by the sessile drop method in a wide range of alcohol and Triton X-165 concentration was studied by Zdziennicka (2010a) which is shown in figure 2.6.

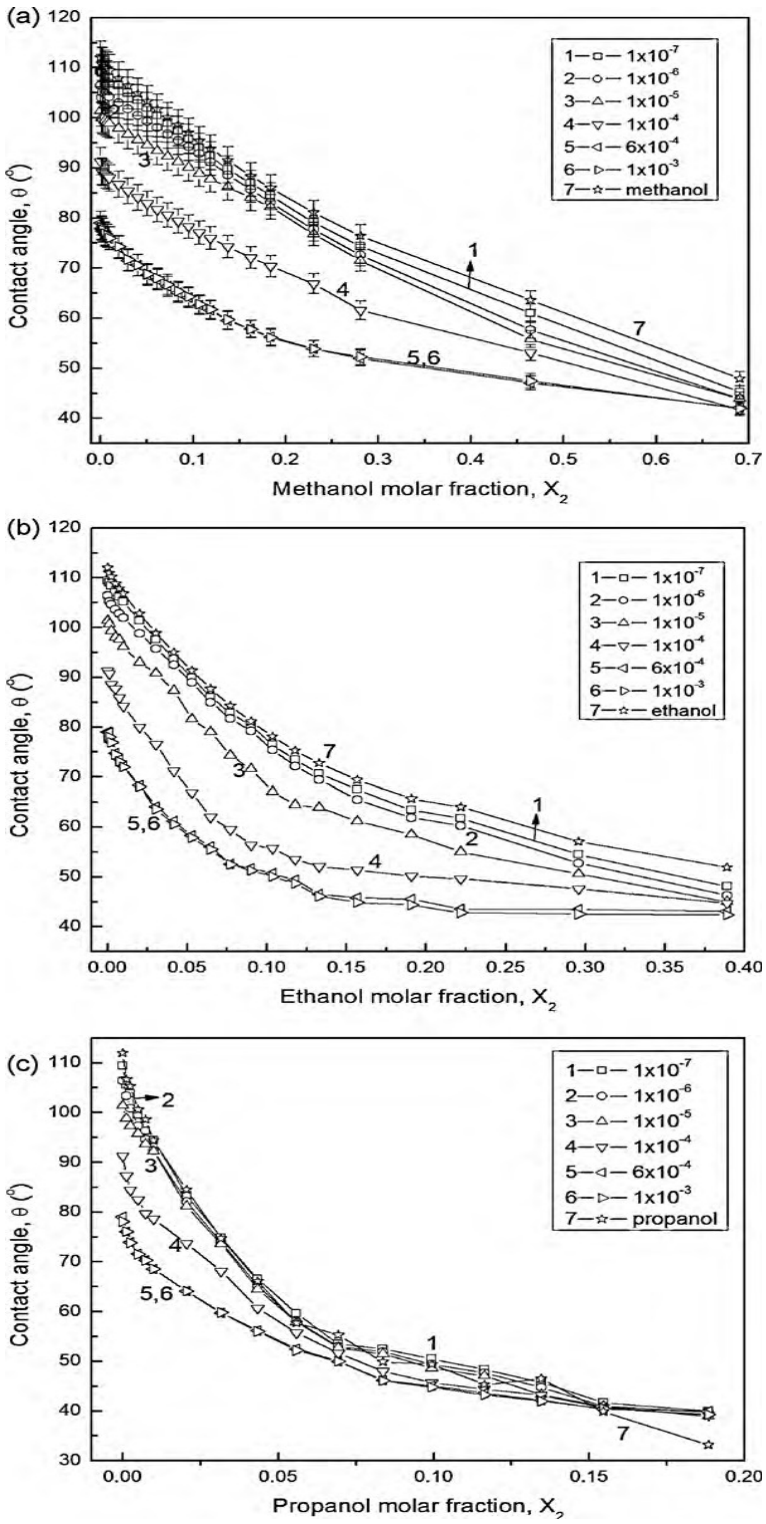


Figure 2.6(a). Dependence between the contact angle (θ) in the system PTFE–solution–air for aqueous solutions of TX-165 mixtures with methanol and alcohol molar fraction (X_2). Curves 1–6 correspond to the constant TX–165 concentration equal to 1×10^{-7}, 1×10^{-6}, 1×10^{-5}, 1×10^{-4},

6×10^{-4} and 1×10^{-3} M, respectively, curve 7 corresponds to pure methanol. (b) Dependence between the contact angle (θ) in the system PTFE–solution–air for aqueous solutions of TX-165 mixtures with ethanol and alcohol molar fraction (X_2). Curves 1–6 correspond to the constant TX-165 concentration equal to 1×10^{-7}, 1×10^{-6}, 1×10^{-5}, 1×10^{-4}, 6×10^{-4} and 1×10^{-3} M, respectively, curve 7 corresponds to pure ethanol. (c) Dependence between the contact angle (θ) in the system PTFE–solution–air for aqueous solutions of TX-165 mixtures with propanol and alcohol molar fraction (X_2). Curves 1–6 correspond to the constant TX-165 concentration equal to 1×10^{-7}, 1×10^{-6}, 1×10^{-5}, 1×10^{-4}, 6×10^{-4} and 1×10^{-3} M, respectively, curve 7 corresponds to pure propanol (Zdziennicka, 2010a).

Taking into account the wide applications of Tritons in cosmetics industry and the fact that PTFE and PMMA are frequently used as a model of human skin wettability, they have find out a relationship not only between the wettability of these solids by aqueous solutions of these mixtures and the total adsorption of surfactant mixtures at water–air and PTFE (PMMA)–water interfaces but also between their wettability and the composition of the surface layer and bulk phase Zdziennicka, (2010b).

2.1.2.2. Effect of Electrolytes on Wetting Behavior of Surfactant Solutions

There are some of the literatures available on wetting behaviour of single surfactant in presence of electrolyte solutions (Radulovic et al., 2009(a); Ghosh Chaudhuri and Paria, 2009) and mixtures of surfactant in presence of electrolyte solutions (Ghosh Chaudhuri et al., 2012) on hydrophobic surfaces. The wetting and spreading behavior of Triton X-100, trisiloxane superspreader, Silwet® L-77 on smooth silicon wafers coated with number of polymers, Parylene (polyxylylene polymer), Cytop and Teflon surfaces has been compared by Radulovic et al. (2009a) and found that, Silwet® L-77 shows better wetting properties, in compare to Triton X-100. They have also investigated the effect of change in pH by addition of acetic acid of surfactant solutions on wettability of polymer coated surfaces. However, wetting ability of Silwet® L-77 drastically reduced with the addition of acetic acid. On the other hand, Triton X-100 was not affected by the addition of acid and exhibited the same spreading behaviour as in water-based solutions.

Ghosh Chaudhuri and Paria (2009) have studied the effect of different mono-valent and di-valent electrolytes on CTAB and SDBS solution wetting and spreading behavior on PTFE surface. They observed that similar to the wetting ability of high surfactant concentration in the

absence of electrolytes can be achieved even for very dilute ionic surfactant solution by adding electrolytes. There also present a significant effect of the valance of counter ion for ionic surfactants for reducing surface tension and contact angle at very low surfactant concentration. The effect of two different electrolytes as additives in the presence of cationic (cetyltrimethylammonium bromide, CTAB) and nonionic (Igepal CO-630) surfactant mixtures on the wetting of a low energy PTFE (polytetrafluoroethylene) surface has been studied by Ghosh Chaudhuri et al. (2012). The cationic–nonionic mixed surfactant system showed a synergetic behavior and a maximum synergism was observed for the mixed surfactant in the presence of electrolytes. The addition of electrolytes in the mixed surfactant solution increases the wettability by achieving minimum contact angle (74.6°) at the PTFE–water interface and reduces the consumption of surfactants up to 85% compared to the pure CTAB.

2.1.3. Effect of Mixed Surfactant Solutions on Wetting

Wetting and spreading processes which involve surfactant solutions are widely used in numerous industrial and practical applications nowadays. The performance of different single surfactants may vary significantly and so far superspreader solutions consider mainly mixed surfactant, show the most promising spreading ability. The addition of mixture of surfactants to water was proven to enhance wetting, even on hydrophobic surfaces, on which conventional surfactants seem to have little or no effect.

There are some literatures documented on the wetting behavior of different binary mixture of anionic- anionic surfactant (Zdziennicka et al., 2003), cationic- cationic surfactant (Szymczyk et al., 2006), cationic-nonionic surfactant (Szymczyk and Janczuk, 2006), and nonionic- nonionic surfactant (Szymczyk and Janczuk, 2007) on hydrophobic surfaces. There also some studies available on the wetting behavior of mixture of ternary surfactant system (Szymczyk and Janczuk, 2010; Szymczyk, 2011) on PTFE surfaces.

Advancing contact angle (θ) measurements were carried out on mixtures of aqueous solutions of sodium dodecyl sulfate (SDDS) and sodium hexadecyl sulfonate (SHDSs) on polytetrafluoroethylene (PTFE) by Zdziennicka et al. (2003) and are shown in figure 2.7.

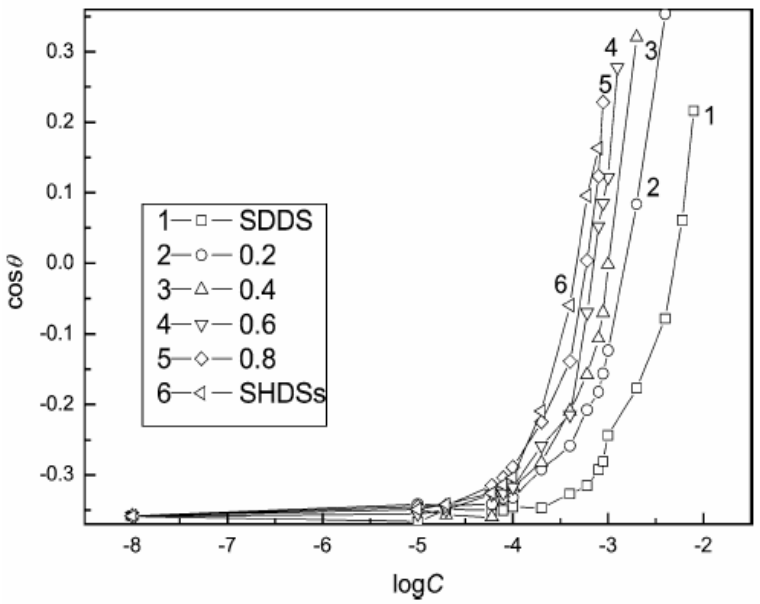


Figure 2.7 The relationship between cos θ (θ—contact angle) and logarithm *C* for different values of the mole fraction (α) of SHDSs in SDDS + SHDSs mixture, where *C* is the total concentration of the mixture (Zdziennicka et al., 2003).

The dependence of cos θ on the monomer mole fraction of SHDSs in the mixture of the surfactants (α) for aqueous solutions of mixtures at concentrations corresponding to the critical micelle concentration (CMC) had a maximum at α = 0.2. the excess concentration of surfactants at the solid–aqueous solution interface to the excess of their concentration at the aqueous solution–air interface was calculated on the linear relationship exist between the adhesion tension and surface tension of aqueous solutions of surfactant mixtures at a given α, and that the slope of the obtained straight lines was equal to −1, which suggests that the surface excess of the surfactant concentrations at the PTFE–solution interface is the same as that at the solution–air interface for a given bulk concentration of the surfactant mixtures.

Szymczyk et al. (2006) studied the effect of cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPyB) and their mixtures on wettability of polytetrafluoroethylene (PTFE) and polymethyl methacrylate (PMMA) surfaces. They found that wettability of PTFE and PMMA depends on the concentration and composition of aqueous solution of CPyB and CTAB mixtures, and there is a deviation from the linear relationship between the contact angle and the mixture composition at a concentration close to and higher than CMC; however, no synergism in wettability is observed. Similarly for PTFE and PMMA there is a linear relationship between the adhesion tension and surface tension of aqueous solution of CPyB and

CTAB mixtures, but the value of the critical surface tension of PTFE wetting is higher than its surface tension, and that of PMMA is lower than PMMA surface tension

Szymczyk and Janczuk (2006) have measured the contact angle of cetyltrimethylammonium bromide, Triton X-100 and their mixtures on PTFE surface and the results indicate that the wettability of PTFE depends on the concentration and composition of the surfactants mixture. There is a minimum of the dependence between contact angle and composition of the mixtures for PTFE for each concentration at a monomer mole fraction of CTAB, $\alpha = 0.2$, which points to the synergism in the wettability of PTFE. Szymczyk and Janczuk (2007) have studied the effect of Triton X-100 and Triton X-165 mixed surfactant on PTFE surface and which is shown in figure 2.8.

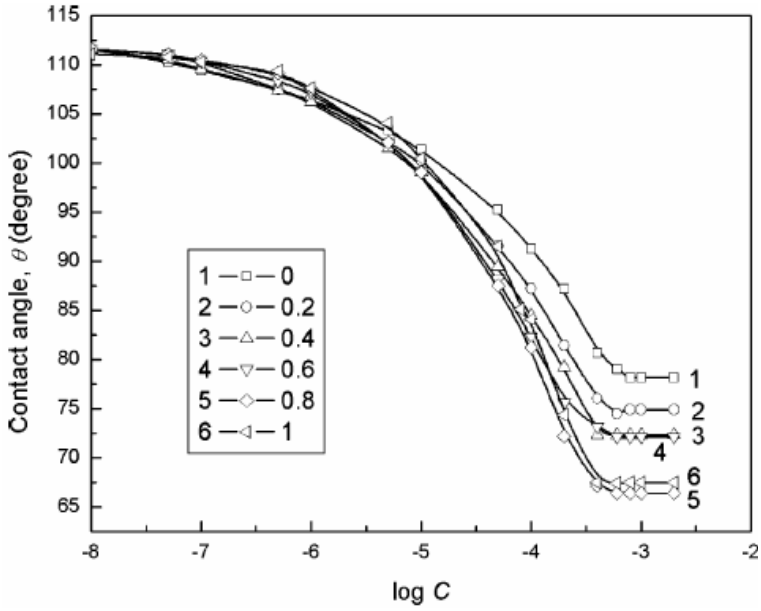


Figure 2.8 Relationship between the contact angle, θ, and log C for different values of the monomer mole fraction of TX100, R, in a TX100 and TX165 mixture (for PTFE), where C is the total concentration of the mixture (Szymczyk and Janczuk, 2006).

Though the wettability depends on concentration and composition of solution, there present synergism on wettability at a monomer mole fraction of Triton X-100, $\alpha = 0.8$ on PTFE. There exists no linear dependence between cos θ and the surface tension whereas linear dependency is there between the adhesional tension and surface tension aqueous solution of Triton X-100 and Triton X-165 mixture for PTFE with the slope -1. Which indicates that the surface excess of the surfactant at the PTFE water interface is same as that at the water-air interface.

Contact angle measurements on poly(tetrafluoroethylene) (PTFE) surface were carried out for the systems containing ternary mixtures of cetyltrimethylammonium bromide (CTAB) and p-(1,1,3,3- tetramethylbutyl)phenoxypoly(ethylene glycols), Triton X-100 (TX100) and Triton X-165 (TX165) by Szymczyk and Janczuk, (2010). They found that there is no linear dependence between the contact angle and the monomer mole fraction of surfactant in binary mixtures of TX100 + TX165 (αTX100 = 0.2), CTAB + TX100 (αCTAB = 0.2) and CTAB + TX165 (αCTAB = 0.2). The addition of a third surfactant to these binary mixtures depend the negative deviation between values of θ and α It means that the synergism in the reduction of the contact angle of water on PTFE surface by aqueous solutions of ternary surfactant mixtures is expected. This synergetic effect was confirmed for all studied ternary mixtures of surfactants by the values of molecular interaction parameters calculated from Rosen's equation on the assumption that binary system is a one surface active agent and compared with the interactions of surfactants at water–air interface. Contact angle measurements on poly(tetrafluoroethylene) (PTFE) and polymethyl methacrylate (PMMA) surface were carried out for the systems containing ternary mixtures of surfactants composed of: p-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycols), Triton X-100 (TX100), Triton X-165 (TX165) and Triton X-114 (TX114), and fluorocarbon surfactants, Zonyl FSN100 (FSN100) and Zonyl FSO100 (FSO100) by Szymczyk, (2011). On the basis of the measured values of the contact angles and their theoretical interpretation, it was concluded that the presence of FSN100 or FSO100 in aqueous solution causes PTFE surface tension decrease in the PTFE–solution drop-air systems because of their absorption into PTFE and the proper orientation of their molecules at interfaces. Because the surface tension of hydrophobic groups of FSN100 or FSO100 is considerably lower than those of Tritons, FSN100 or FSO100 concentration increase causes PTFE surface tension decrease step by step up to some constants values. This also explains why the FSN100 or FSO100 are weak wetting agents why, contrary to aqueous solutions including Triton's, the dependence between adhesional and surface tension of solution including FSN100 or FSO100 can be divided into two linear parts and why the work of adhesion of aqueous solutions of individual FSN100 or FSO100 surfactants and their mixtures with Triton`s to PTFE surface in contrast to Triton`s and their mixtures, is not constant and depends on FSN100 or FSO100 concentration. The proposed changes in PTFE surface tension as the results of FSN100 or FSO100 absorption explain also why in the presence of FSN100 or FSO100 there is no

correlation between critical surface tension of PTFE wetting (γ_C) and work of adhesion of solution to PTFE surface and why there exists a differences between this tension and surface tension of PTFE surface. Studies on wetting of mixed surfactant systems on hydrophobic surfaces are summarized in Table-2.1.

Table 2.1 Previous studies on mixed surfactant system hydrophobic surfaces.

Combination used	**Surfactants used**	**Surface used**	**Reference**
Anionic+Anionic	Sodium dodecyl sulfate and Sodium hexadecyl sulfonate	PTFE	Zdziennicka et al., 2003
Cationic+Anionic	N-dodecyl trimethylammonium chloride, ndodecyl trimethylammonium bromide, sodium 1-decanesulfonate and sodium dodecyl sulphate	Polyethylene (PE)	Wu and Rosen, 2005
Nonionic+Cationic	Triton X-100 and Cetyltrimethylammoniumbromide	PTFE	Szymczyk and Janczuk, 2006
Cationic+Cationic	Cetyltrimethylammonium bromide and Cetylpyridinium bromide	PTFE and PMMA	Szymczyk et al., 2006
Nonionic+Nonionic	Triton X-100 and Triton X-165	PTFE	Szymczyk and Janczuk, 2007
Cationic+Cationic	Dodecylethyldimethylammonium bromide and Benzyldimethyldodecylammonium bromide	PTFE and PMMA	Harkot and Janczuk, 2009

2.2. Wetting of Hydrophilic Surfaces

Wetting of hydrophilic surfaces have many important applications like surface cleaning, oil recovery, forth flotation where it is necessary to wet that surface.

2.2.1. Wetting of Hydrophilic Surfaces by Single Surfactant System

There are some studies documented on the wetting behavior of different single chain cationcs (Hanna and Saleeb, 1980; Eriksson et al., 1996; Koopal et al., 1999; Li et al., 1999; Standnes and Austad, 2000, 2003a,b), anionics (Alexandrova and Grigorov, 1998; Lu et al., 1997a,b; Cipriano et al., 2005), and non-ionic (Scales et al., 1986; Menezes et al., 1989; Oh et al., 2003; Sis and Chander, 2003; Ketelson et al., 2005; Bryant et al., 2006; Zelenev et al., 2011) surfactant systems on hydrophilic surfaces.

2.2.1.1 Wetting of Hydrophilic Surfaces by Nonionic Surfactant Solutions

Hydrophilic (α-quartz) plates has been prepared by reaction of the base solid with trimethylchlorosilane to produce grafted trimethylsilyl groups at the particle surfaces and with thionyl chloride followed by butyl lithium to produce grafted butyl groups at the particle surfaces and these solids designated as m-SiO_2, and b-SiO_2, respectively by Scales et al. (1986). The subsequent change in contact angle of such surfaces exposed to nonionic (ethoxylated nonyl phenol and ethoxylated dodecyl ether type) surfactants has been determined over a four decade range of concentrations of 0.01 to 100 times the critical micelle concentration (CMC) for the surfactant series with a varies in range of wetting angles from 0 to 90. The contact angles measurements made with decane-water-quartz systems indicate an increase followed by a decrease in the contact angle as the concentration of CTAB is increases by Menezes et al. (1989). The angle does not change substantially when SDS is used. The predicted contact angles using only the measured DLVO components of disjoining pressure do not indicate the same trend. The decrease in contact angles at above the CMC can be attributed to the formation of bilayers at the quartz surface. The effect of non-ionic surfactants on surface hydrophilicity and detail reproducibility of die stone for hydrophilic polyvinyl siloxane impression materials. prepared with a polydimethylsiloxane composition and non-ionic surfactants has been examined by Oh et al. (2003). Adsorption and contact angle of single and binary mixtures of sodium oleate and ethoxylated nonylphenol type nonionic surfactants on apatite minerals were also studied by Sis and Chander (2003). The effect of Ca^{2+} ions was investigated in the absence and presence of

nonionic surfactants. The wettability of poly[2-hydroxyethyl methacrylate-co-methacrylic acid] (pHEMA-MAA) soft contact lenses was investigated in the absence and presence of block copolymer surfactants and lysozyme using the sessile drop method. The advancing dynamic contact angles ($\Theta_{w/a}$) values are reported for water as a function of sequential wetting and drying cycles (Ketelson et al., 2005). Wetting alteration of mica surfaces in reservoir with polyethoxylated amine surfactants has been studied by Bryant et al. (2006). The surfactants used were polyethoxylated coconut and tallow amines with chain lengths of 12 and 18 carbons and head groups consisting of two to five ethoxy groups. It was found that the contact angles were in the intermediate to water-wet range if the mica samples were removed from the surfactant solution, rinsed with non-aqueous solvents, and submerged in decane for measurements of water/decane contact angles. The interactions between the water-in-oil, oil-in-water and balanced microemulsions made with ethoxylated alcohol surfactant and d-limonene as the oil phase were diluted with distilled water and 2% KCl solutions with Marcellus shale rock were studied by performing adsorption and wettability measurements (Zelenev et al., 2011). It was discovered that the behavior in adsorption and wetting studies of diluted balanced microemulsion was significantly different as compared to the adsorption from diluted o/w and w/o microemulsions.

2.2.1.2 Wetting of Hydrophilic Surfaces by Anionic Surfactant Solutions

The abilities of three ionic surfactants—sodium methylnaphthalene sulfonate (SMNS), sodium dodecyl sulfate (SDS), and cetyl trimethylammonium bromide (CTAB) to alter the wettability of bitumen-treated glass surfaces was examined by Liu et al. (2011). Surface wettability was characterized by contact angles, and all measurements were carried out under alkaline conditions by having sodium carbonate (Na_2CO_3) dissolved in the aqueous phase. It was found that Na_2CO_3 alone could slightly increase the hydrophilcity of bitumen-treated glass surfaces. With surfactants added to the system, it was demonstrated that SMNS and SDS (both anionic surfactants) were much more effective in enhancing the water wettability of bitumen-treated glass in comparison to CTAB (a cationic surfactant). The ability of methyldodecylbis [2-(dimethyldodecylammonio) ethyl] ammonium tribromide, a trimeric cationic surfactant to alter the wettability of water-wet and oil-wet mica mineral surfaces has been studied by Zhang et al. (2012) shown in figure 2.9. The contact angle data of the solid–liquid interface in oil/water/solid three-phase system show that the trimeric cationic surfactant, when compared with single- and

double-chain cationic surfactant, is a more effective wetting agent for water-wet and oilwet mica surfaces at lower concentration.

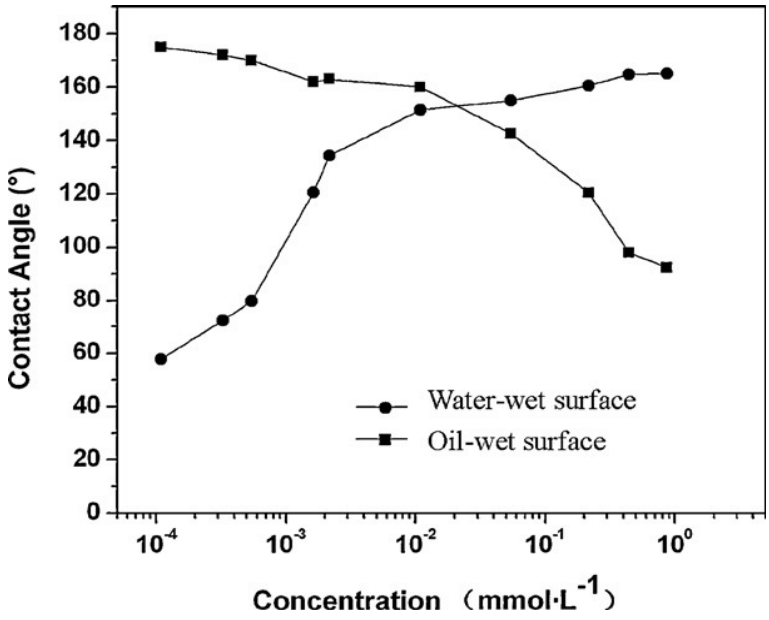


Figure 2.9 Variation of the contact angle with the 12-2-12-2-12 aqueous solution concentration on water-wet and oil-wet mica surfaces (Zhang et al., 2012).

Measurements by atomic force microscopy (AFM) show that the surfactant molecules have formed a monolayer to reverse the wetting properties. On the water-wet surface, the surface is suffused with negative charge, which could attract the cationic head of surfactant, and leave the hydrophobic tails exposed. In contrast, on the oil-wet surface, the hydrophobic tails were attracted by hydrophobic interactions to the oil film between the surfactant and the crude oil. The hydrophilic heads were left outside to form a hydrophilic layer, which could explain the wettable to hydrophilic trend. Alteration to the degree of wettability is mainly dependent on the adsorption areas of the surfactant. The data show that the ability of the trimeric cationic surfactant affect the wettabil ity is independent of surface tension.

2.2.1.3 Wetting of Hydrophilic Surfaces by Cationic Surfactant Solutions

The adsorptionn and wetting charactists of a sample of precipitated hyroxyapatite (HAP) and sample of natural carbonate-fluorapatite francolite in contact with cationic surfactants CTAB and CPB at constant pH temperature and ionic strength was studied by Hanna and Saleeb (1980). The wetting behavior of cationic CTAB surfactant solution on freshly cleaved mica sheet in the concentrations ranges from 10^{-7} to 1.6 x 10-^{3} M was studied in wilhelmy plate method by Eriksson et al. (1996). They found that the contact angle similar to equilibrium wetting tension

first decreases with concentration due to solid-vapor monolayer adsorption, reaches a minimum at 2.4 x 10^{-5} M (contact angle 73º), and then increases up to 3 x 10^{-4} M due to solid/liquid bilayer adsorption as shown in figure 2.10.

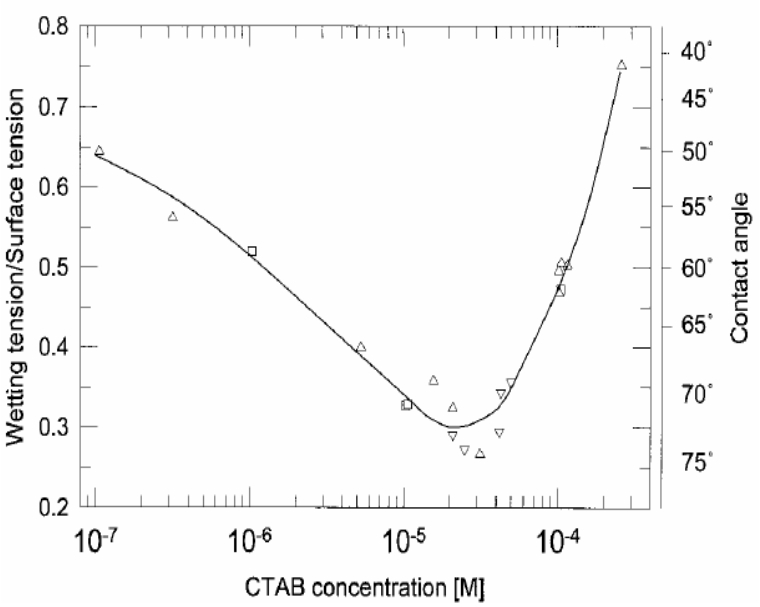


Figure 2.10 Equilibrium contact angles for CTAB solution on mica as a function of CTAB concentration up to 3 x 10^{-4} M, calculated from wetting tension data (Eriksson et al., 1996).

The effect of lowering of the liquid level by evaporation on the measured values of the advancing wetting tension is calculated by Eriksson (1997) and to be able to account for most of the change with time of the advancing wetting tension concerned with the adsorption of hexadecyltrimethylammonium bromide (CTAB) on mica, using rates of evaporation (≈ 0.07 mm/h) measured for that setup. Contact angle, colloid stability and flotation measurements have been carried out for silica as a function of the concentration of cationic dodecyl and cetyl pyridinium chloride (DPC and CPC), and dodecyl trimethyl-ammonium bromide surfactants at different pH and calcium salt concentrations and the results are compared with surfactant adsorption and surface charge isotherms by Koopal et al. (1999). Contact angles of surfactant solutions of known pH and salt concentration were measured on the oxidised silicon wafer surface with both the sessile drop and the pendant bubble method using tioning. a KRUSS contact angle microscope with goniometer. The nature of adsorbed cationic amphiphiles at the mica/solution interface was studied by XPS and contact angle measurements (Li et al., 1999). The contact angle of water drops placed on the adsorbed surface showed a gradual decrease with the elapse of time due to the dissolution of adsorbed surfactant into the water drop; however, the

decrease was not observed for those mica surfaces when aged for more than 3 days in the adsorption bath. Standnes and Austad (2000) and (2003a) have studied wettability alteration (oil-wet to water-wet) in chalk using four different types of cationic surfactants like C_{10}TAB, C_{12}TAB, C_{14}TAB and C_{16}TAB. And found that the suggested mechanism for the spontaneous imbibition of water into oil-wet carbonate rock by means of a wettability alteration using cationic surfactant. Standnes and Austad (2003b) have also studied nontoxic low-cost amines as wettability alteration chemicals in carbonates improve the oil recovery from low temperature, oil-wet/neutral-wet, fractured carbonate reservoirs.

A new method for the characterization of the wettability of opaque solid surfaces by measuring (a) the lifetime of thin liquid films, (b) the kinetics of expansion of the three-phase contact (TPC), (c) the equilibrium contact angle is developed by Alexandrova and Grigorov, (1998). The method is tested with galena xanthate and copper mineral pyrite Aerodri 104 systems. Lu et al. (1997a,b) investigated the hydrophobic properties of apatite with contact angle experiments at different concentrations of oleate. In their experiments, the apatite surface was first conditioned with oleate solution for 20 min at pH 9.0 and then the surface was rinsed with distilled water. One drop of distilled water of pH 6 was introduced on apatite surface and advancing contact angle of distilled water was measured. The maximum advancing contact angle of 100º was obtained at 20–30 mg/l sodium oleate concentration. Further increase in concentration led to a decrease in advancing contact angle. They proposed the formation of a second layer of surfactant in reverse orientation to explain the observations. The differences in concentration where maximum contact angle was observed by these investigators and the present study could be explained by variation in the methodology. These investigators used distilled water instead of the conditioning solution on solid surface and measured advancing contact angle instead of contact angle of the free drop. The advancing and receding contact angles of 1,2-dimethyl-3-*N*-hexadecyl imidazolium tetrafluoroborate (Im BF4) as a function of concentration has been measured on pre-equilibrated mica surfaces by Cipriano et al. (2005). They found that the contact angles of Im BF4 surfactant solutions wetting pre-equilibrated mica surfaces show surfactant adsorption occurring at 10^{-6} mol/L. At 7×10^{-5} mol/L, a maximum in the hydrophobicity of the surface is measured, with a contact angle of 84◦ ±2º. The results show that the Im BF4 surfactant adsorbs onto the mica surface and produces a hydrophobic surface, similar to the behavior of cetyl trimethyl ammonium bromide (CTAB).

2.2.1.4 Wetting of Hydrophilic Surfaces by Double Chain Surfactants

There are some of the researches documented on the wettability of double chain surfactant (Pyter et al., 1982; Harkot and Janczuk, 2008) dimeric cationic gemin surfactants (Bi et al., 2005; Pisarcik et al., 2005; Cao et al. 2006; Basch and Strnad, 2011) anionic gemin surfactants (Ao et al., 2009), zwitterionic gemini surfactants (Seredyuket al., 2002) on hydrophilic surfaces.

The role of surfactant adsorption in the wetting of relatively low-energy solids evaluated from contact angle measurement using various aqueous surfactant solution-solid combinations has been studied by Pyter et al. (1982). Analysis of the resulting data indicates that with many systems, pure liquids of low surface tension and aqueous surfactant solutions having the same surface tension do not produce the same contact angles; pure liquids often are better wetting agents. For hydrocarbon surfactants these effects are more significant for semipolar solids such as polymethyl methacrylate than for nonpolar solids. Harkot and Janczuk (2008) studied wettability of anionic sodium bis(2-ethylhexyl) sulfosuccinate on Glass and PMMA surfaces and found that there exists a linear relation between adhesional tension versus surface tension. There also a study related to the wettability of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) on PTFE surface (Harkot and Janczuk, 2007). Basch and Strnad (2011) have investigated wetting abilities of alumina powder by powder contact angle method put the powder into the measuring cylinder of the tensiometer and making contact with the liquid phase. They measured the sample mass change as a function of time. Using N-heptane with its excellent wetting abilities the contact angle is close to zero and cos θ was estimated to be 1.

Pisarcik et al. (2005) have studied contact angle of cationic gemini surfactant with different spacer 2, 4, and 6 in order to determined area per molecule at hydrophobic solid – water interface and found that the surfactant molecules present at the liquid/hydrophobic solid interface are almost three times as closely packed as those at the liquid/air interface. Adsorption of a [C_{12}-6-C_{12}]Br_2 gemini surfactant on silica and its effect on wettability has been studied by Cao et al. (2006) and is shown in figure 2.11. Initially at low surfactant concentration there is a random distribution of surfactant molecules on the surface of silica with the conformation of lying parallel to the substrate plane facing their hydrophobic tails exposed towards air. With the increase in surfactant concentration contact angle also increases.

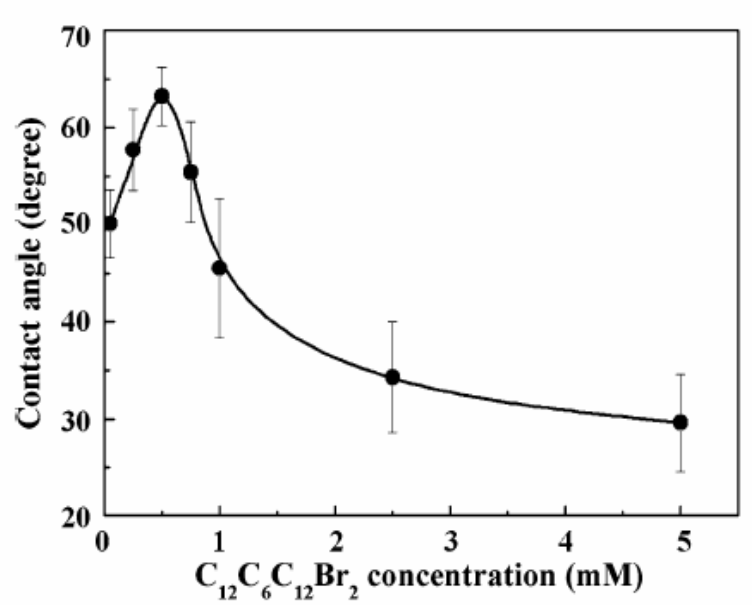


Figure 2.11 The initial static contact angles of silica substrates treated with C_{12}-$C_6C_{12}Br_2$ solutions of different concentration. The error bars indicate the degree of reproducibility of the measurement (Cao et al., 2006).

Once the critical surface aggregation concentration reached maximum contact angle observed and above that due to formation of circular islands, then to semicontinuous islands, and finally to the two-bilayered structure, the contact angle values again starts decreasing. Similar expression also observed when comparison of imidazolium gemini surfactant [C_{12}-$_4$-C_{12}im]Br_2 on silicon wafer was done with its monomer [C_{12}mim]Br by Ao et al. (2009). Below the critical surface aggregation concentrations (CSAC), both surfactant molecules are adsorbed with their hydrophobic tails facing the air. But above the CSAC, [C_{12}-4-C_{12}im]Br_2 molecules finally form a bilayer structure with hydrophilic head groups facing the air, whereas [C_{12}mim]Br molecules form a multilayer structure, and with increasing its concentration. The layer numbers increase with the hydrophobic chains and hydrophilic head groups facing the air by turns.

The contact angle of drops of aqueous solutions of a series of zwitterionic Gemini surfactants on paper surfaces as porous substrate was determined by means of a dynamic adsorption tester by Seredyuk et al. (2002). The concentrations used were 0.01 (close to the CMC), 0.1 and 1 mM and found that only the highest concentration which is around 100 times the CMC gives a pronounced reduction in contact angle under the dynamic conditions that prevail during wetting on a penetrating substrate such as paper. The additional factor that may

contribute to the poor performance in the wetting experiment is the very low CMC of the Gemini surfactants which leads to low unimer concentrations.

2.2.1.5 Wetting by Bio-surfactants

The wetting properties of biologically produced rhamnolipids (R_L), advancing contact angles of the aqueous solutions of the R_L mixture of R_1 and R_2 in a ratio of $R_2/R_1 = 1.1$ were measured as a function of surfactant concentration on hydrophilic glass and gold surfaces by Ozdemira and Malayoglu (2004). For a comparison of the wetting performance, sodium dodecyl sulfate (SDS) was chosen as the reference surfactant. At low surfactant concentrations (R_L concentration $< 3 \times 10^{-5}$ M, SDS concentration $< 3 \times 10^{-4}$ M) contact angle (θ) varied in a certain range depending on the character of the surfactant interactions with the surface. On hydrophilic surfaces a steady decrease in adhesion tension was observed with both surfactant solutions.

2.2.2 Effect of Alcohols on Wetting Behavior of Surfactant Solutions

Zdziennicka and Janczuk (2010) have studied the wettability of aqueous solution of Triton X-100 with methanol, ethanol and propanol mixtures and Triton X-165 with the same alcohols on quartz surface. The positive slopes of the linear dependence between the adhesional tension and surface tension of solutions indicate that adsorption of the surface active agents at quartz–water interface probably becomes negative because of the presence of strongly ordered water film on this surface, but it is probably positive at quartz/monolayer water film–water interface.

2.2.3 Effect of Mixed Surfactant Solutions on Wetting

Szymczyk and Janczuk (2008) measured the contact angle of surfactants, Triton X-100, Triton X-165 and their mixtures on Glass surfaces. Though the wettability depends on concentration and composition of solution, there present synergism on wettability at a monomer mole fraction of Triton X-100, $\alpha = 0.2$ and 0.4 on Glass surface and which is shown in Figure 2.12. There also no linear dependence present between $\cos \theta$ and the surface tension of aqueous solutions of surfactant mixtures, but a linear dependence exists between the adhesional tension and surface tension for glass, having slops of which are positive in the range of 0.43-0.67 indicates the surface excess of the surfactant concentration at the glass solution interface is not same as that at the solution-air interface (Szymczyk and Janczuk, 2008).

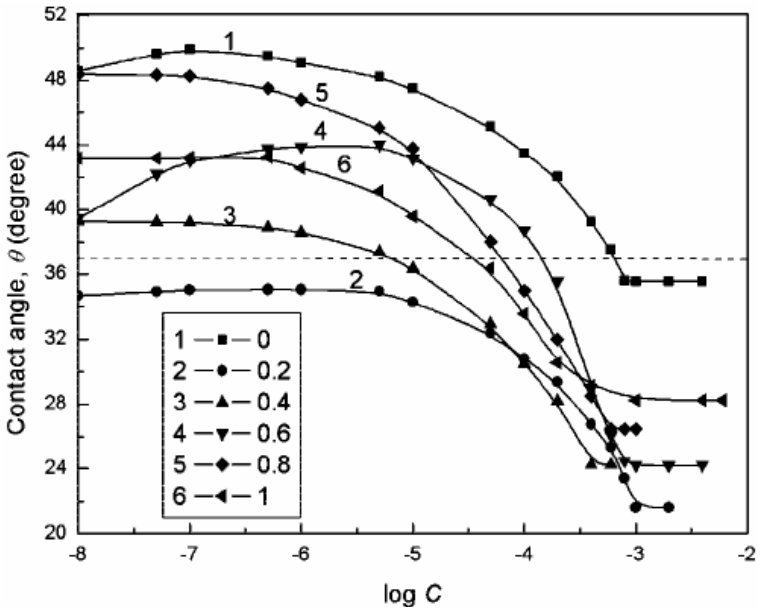


Figure 2.12 Relationship between the contact angle, θ, and logarithm C for different values of the monomer mole fraction of TX 100, α, in TX100 and TX 165 mixtures, where C is the total concentration of the mixture (Szymczyk and Janczuk, 2008).

2.3 Concluding Remarks

From the review of literature it has been found that there are numerous literatures available on adsorption of surfactants at hydrophilic surfaces but limited on hydrophobic PTFE surface, and none on effect of electrolytes on PTFE surface. It has also been found that several studies are available on adsorption behavior on synthetic surfactants but limited on natural surfactants. Regarding the wetting behavior of synthetic surfactants, there are limited studies on Gemini surfactants and none on double chain cationic surfactants. Moreover, there is none on wetting behavior of synthetic-natural mixed system. Hence, this study is mainly focused to carry out some experimental works on the above mentioned areas to get some new findings.

Chapter 3

Effect of Electrolyte Solutions on the Adsorption of Surfactants at PTFE–Water Interface

Chapter 3

Effect of Electrolyte Solutions on the Adsorption of Surfactants at PTFE–Water Interface

3.1 Introduction

Surfactant adsorption at solid-liquid interfaces has been extensively studied by many researchers for a long period of time because of its versatile applications. The adsorption of surfactants at the interfaces is always there whenever they are used in different applications. Surfactants can change the solid surface property from hydrophilic to hydrophobic and vice versa by adsorption. There are many studies available on the surfactant adsorption at hydrophilic surfaces, compared to only a few at hydrophobic surfaces. Surfactant adsorption at hydrophobic solid-water interfaces has applications such as wetting (Janczuk and Chibowski,1985), stabilization of polymer suspension (Romero-Cano et al., 1998), surface cleaning (Wu et al.,2009), etc. To see the effectiveness of these applications there are also some studies available on contact angle and wetting properties of different hydrophobic polymer surfaces such as polytetrafluoroethylene (PTFE) (Zdziennicka et al., 2003; Szymczyk and Janczuk, 2006; Szymczyk and Janczuk, 2007; Zdziennicka and Janczuk, 2008; Chaudhuri and Paria, 2009) and both PTFE and polymethyl methacrylate (PMMA) (Szymczyk et al., 2006; Harkot and Janczuk, 2010) where surfactant adsorption is inherently involved. In general, hydrophobic or polymer surfaces have low surface energy and are difficult to suspend or wet by aqueous media for different applications. The adsorption of surfactants on hydrophobic surfaces overcomes those difficulties by changing the surface properties. In this regard, apart from the adsorption at solid-liquid interface, surface tension of the aqueous solution which is related to the adsorption at air-liquid interface is equally important. The effect of ionic strength or electrolytes can significantly influence the critical micellar concentration (CMC), surface tension value at CMC, and adsorption densities at air-liquid and solid-liquid interfaces which may have great importance in many applications.

Surfactant adsorption studies on polymer surfaces are mainly reported at PTFE (Yao and Straus, 1991; Yao and Strauss, 1992; Desai and Dixit, 1996; Vanjara and Dixit, 1996; Dixit et al., 2002), polystyrene (Romero-Cano et al., 1998; Connor and Ottewill, 1971; Zhao and Brown, 1996; Martin-Rodriguez et al., 1997; Romero-Cano et al., 1998), polyvinyltoluene (PVT)

(Santhanalakshmi and Balaji, 2000), and PMMA (Steinby et al., 1993) surfaces. Dixit and co-workers studied single cationic surfactants (Vanjara and Dixit, 1996) and cationic-nonionic mixed surfactants systems on PTFE surface (Desai and Dixit, 1996; Dixit et al., 2002). In a single cationic surfactant system they have studied the effects of chain length of alkyltrimethyl ammonium bromide and pyridinium chloride surfactants. The isotherm consisted of two plateau regions due to formation of hemimicelle. In the cationic-nonionic (CTAB-NPn) mixed surfactant system adsorption of either cationic or nonionic was enhanced below the CMC and adsorption of CTAB decreased with the increase in mole fraction of nonionic surfactants (NPn) above the CMC due to formation of mixed micelle (Desai and Dixit, 1996). Connor and Ottewill (1971) showed the formation of hemimicelle for cationic surfactant on polystyrene surface; they suggested that the particles have two types of sites for adsorption: charged sites which interact with the cationic headgroup of the surfactant and adsorption through tailgroup on the hydrophobic sites. The adsorption of nonionic nonylphenol polyethylene oxide of different chain lengths on PMMA surface shows Langmuir isotherm due to the formation of monolayer (Steinby et al., 1993).

Regarding the effect of electrolytes on surfactant adsorption, it is observed that although there is much literature available on hydrophilic surfaces (Subramanian and Ducker, 2000; Atkin et al., 2003; Paria et al., 2005; Paria and Yuet, 2006; Howard et al., 2009), there is not any on hydrophobic surfaces. Atkin et al. (2003) found the addition of electrolytes shifted the adsorption isotherm of CTAB toward lower concentration with increase in maximal surface excess at silica-water interface and Br- ion was more effective to increase the surface excess of CTAB than that of Cl^- to the CTAC system. Paria and Yuet (2006) concluded the adsorption of cationic surfactant on negatively charged hydrophilic surface (sand) linearly increased with the increasing electrolyte concentration at a constant surfactant concentration below the CMC mainly due to reduction of repulsion between the surfactant headgroups. Also, between the two forces (i) attraction between the solid surface and surfactant headgroups and (ii) repulsion between the headgroups, the latter was predominant for increasing the surface excess in the presence of electrolytes. Howard et al. (2009) showed that there exists a common intersection point (CIP) at which a particular surfactant concentration below this point an increase in electrolyte concentration reduced surfactant surface excess, and at concentrations above this point an increase in electrolyte concentration led to an increase in surfactant surface excess.

From the literature it is clear that limited studies are available on the adsorption of surfactants (kinetics and isotherm) at PTFE surface. Although there are some studies available on the effect of electrolytes on surfactant adsorption at the hydrophilic solid-liquid interface, there are no studies on PTFE or other hydrophobic surfaces to the best of our knowledge. In this chapter, we have studied the adsorption kinetics and the isotherms of three different surfactants (anionic, SDBS; cationic, CPB; and nonionic, TX-100) at PTFE surface. In addition, electrolytes effects have also been studied on the adsorption of anionic and cationic surfactants at PTFE-water interface. The objective of this section is to study the adsorption behavior of surfactants in the presence of electrolytes to reduce the surfactant consumption. Food processing and many other industrial operations use PTFE-coated reactors and pipes; regular cleaning of those is essential, especially in food processing operations. The presence of electrolyte along with the surfactants in the cleaning process may reduce the consumption of surfactant along with the increase in adsorption and wetting properties. In many cases, after the cleaning process surfactants are disposed in the environment; in this situation, less consumption of surfactant may also reduce environmental problems.

3.2 Materials and Methods

3.2.1 Materials

Triton X-100 (TX-100; 99% purity) was purchased from Loba Chemicals Pvt. Ltd., India. Cetylpyridinium bromide (CPB, 99%) from Rankem, India and sodium dodecylbenzene sulfonate (SDBS) of technical grade (Cat no. 28 995-7) from Sigma-Aldrich chemicals, Germany were purchased and used without any further purification (structures are shown in Figure 3.1). The electrolytes NaCl and Na_2SO_4 were purchased from Rankem and $CaCl_2$ was from Merck, India. The PTFE powder used for adsorption experiments was purchased from Pragati Plastics Pvt. Ltd., Delhi, India. Aqueous solutions of individual surfactants were made by ultrapure water (Sartorius, Germany) of 18.2 MΩ·cm resistivity, 71.5 mN/m surface tension, and 6.5–7 pH at 25 ± 0.5 °C. For all the experiments, a single surfactant solution of desired concentration was prepared by diluting a concentrated stock solution.

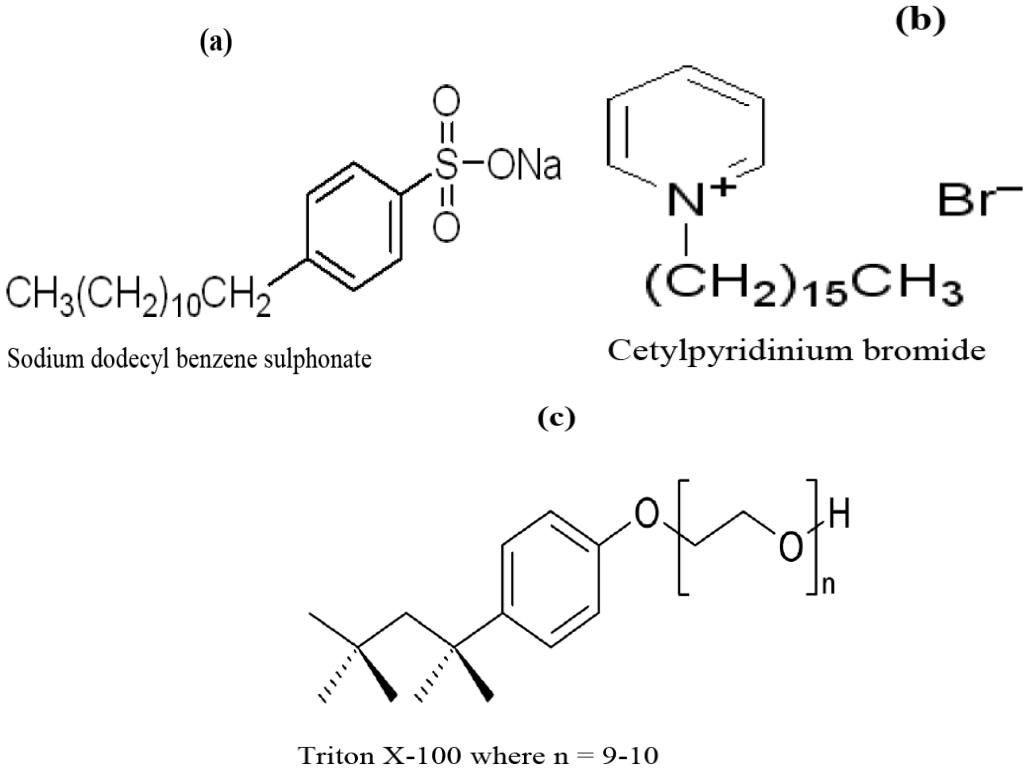


Figure 3.1 Structures of the surfactant molecules: (a) SDBS, (b) CPB, (c) TX-100,

The particle size of the PTFE powder was measured using a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., U. K.) and found that the average particle size 115.7 μm. The zeta potential of PTFE powder was measured by equilibrating 5 mg of powder in 50 mL of 0.01 M KCl solution using Zetasizer Nano ZS (Malvern, U.K.). The zeta (ξ) potential was calculated from the electrophoretic mobility using Smoluchowski's equation and found to be -4.82 mV. The specific surface area (BET) of the PTFE powder was measured twice by N_2 adsorption-desorption studies at liquid nitrogen temperature (-195.8 °C) using Autosorb-1 (Quantachrome, USA) and the average value was found to be 4.3 m^2g^{-1}. Prior to the analysis, samples were degassed at 200 °C. Low nitrogen adsorption at relative pressure (P/P_0) values <0.2 indicates the absence of microporosity, which is also reflected in the low value of the BET surface area, 4.3 m^2g^{-1}.

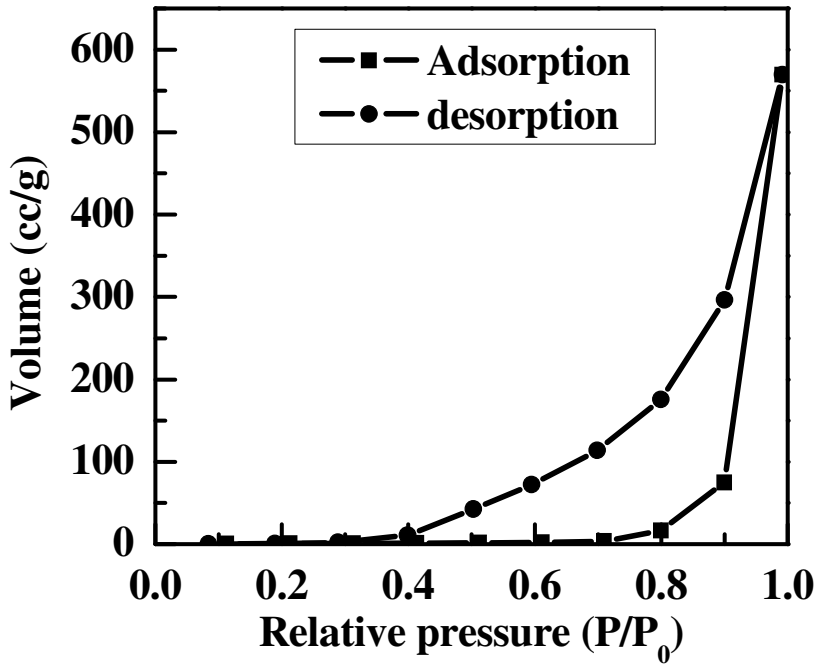


Figure 3.2 N_2 adsorption–desorption isotherm of PTFE powder

Low nitrogen adsorption at relative pressure (P/P_0) values <0.2 indicates the absence of microporosity, that is also reflected in the low value of the BET surface area, 4.345 m^2g^{-1}. The presence of a hysteresis loop in the isotherm indicates the presence of mesoporosity. Furthermore, the adsorption limit is not well defined at relative pressures close to one and the isotherm rises rapidly near $P/P_0 = 1$ which is an indication of the presence of macroporosity in the material.

3.2.2 Methods

3.2.2.1 Measurement of Surface Tension and CMC

All the surfactant solutions were prepared freshly just before the measurements. The solutions of desired concentration were prepared from a 10 mM stock solution using a 100 ml volumetric flask. The surface tension of aqueous surfactants solutions (0.0005 – 2 mM) were measured by the Wilhelmy plate method using a surface tensiometer (Data Physics, Germany, DCAT-11EC) at 25 ± 0.5 °C, the temperature was maintained using an external constant temperature water circulator. The motor speed of 1 mm/sec and immersion depth of the platinum plate in the surfactant solution maintained was 3 mm. After measurement of each concentration the plate was cleaned with water, acetone and finally burned in alcohol flame. The CMCs of Triton X–100

(TX–100), Igepal CO 630 were found 0.15 and 0.08 mmol/L respectively by the surface tension measurement technique.

3.2.2.2 Surfactant Adsorption Kinetics and Isotherm on PTFE Surface

For the adsorption experiments a volume of 10 ml surfactant solution having different concentrations (0.02 – 2 mM for the isotherm and 0.05 mM for kinetics) were taken in 60 mL plastic bottles, and 0.1g of PTFE powder was used for all the experiments. The bottles were shaken well for 2 hrs at 25 ± 0.5 °C on an incubator shaker. PTFE particles were separated from the mixture by centrifugation at 5000 rpm. The concentrations of the surfactants solution before and after the adsorption were determined by an UV–vis spectrophotometer (UV-3600, Shimadzu Scientific Instruments, Japan) using their respective calibration curves (Absorbance vs. concentration) constructed from the known concentrations.

The experiments were repeated at least thrice and the average data were plotted. The amount of surfactant adsorbed was determined by the following equation.

$$\Gamma = \frac{(C_i - C_{eq})V}{m \times 1000} \tag{3.1}$$

Where C_i and C_{eq} are the initial and equilibrium concentrations (mM), V is the volume of surfactant solution (mL) and m is the mass of the adsorbent (g).

3.3 Results and Discussion

3.3.1 Adsorption Kinetics

Adsorption kinetics of three different surfactants (CPB, SDBS, and TX-100) at 0.2 mM concentration at PTFE-water interface are presented in Figure 3.3a. The adsorption kinetics are studied to know the rate as well as equilibrium time for the adsorption process. At very low surfactant concentration the amount of surfactant adsorbed as well as the differences among the surfactants are less, hence the concentration was chosen for kinetics where the difference is more.

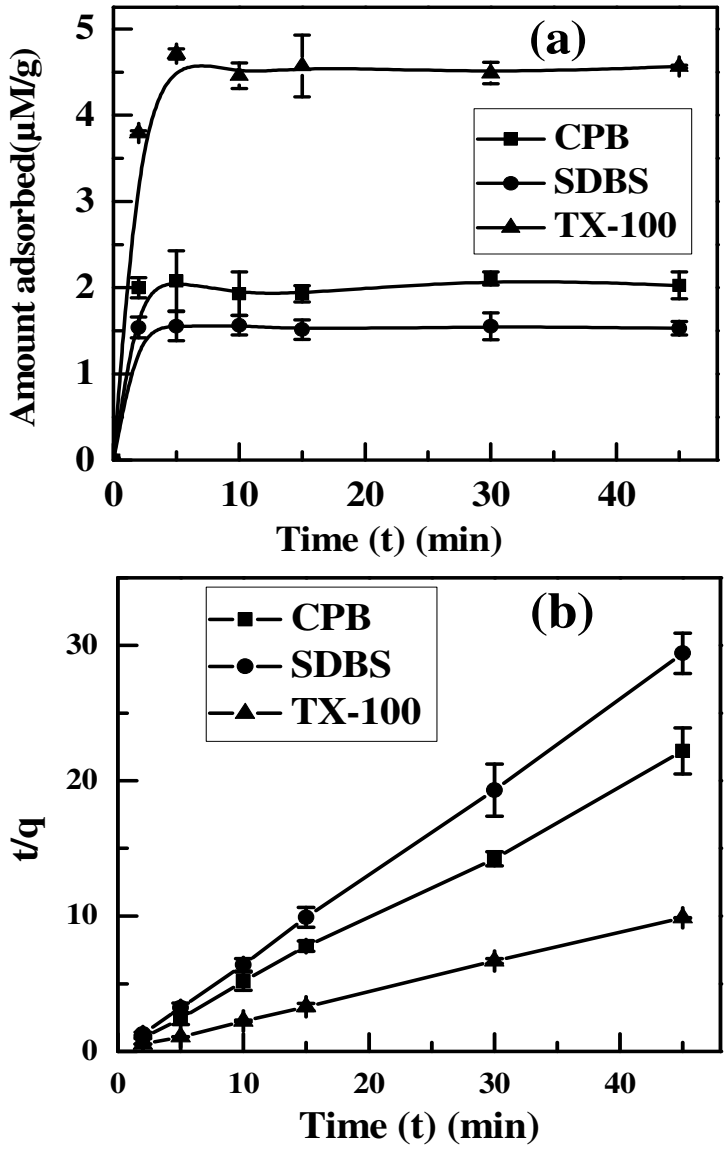


Figure 3.3 (a) Adsorption kinetics of CPB, SDBS, and TX–100 on PTFE powder using 0.2 mM surfactant concentration. (b) Linear fitting of pseudo–second–order kinetics.

It is found from the figure that within 10 min all three surfactants reached equilibrium and the rate of adsorption is also very fast. Figure 3.3a shows that at 0.2 mM concentration the surfactants are following the order of amount adsorbed at equilibrium TX-100 > CPB > SDBS. To know the rate at which adsorption takes place there are generally two commonly used kinetic models, i.e., pseudo-first-order and pseudo-second-order, to identify the nature of surfactant adsorption. The pseudo-firstorder kinetics can be presented as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3.2)$$

The equation (3.2) then integrated for the conditions $t = 0$ to t and $q = 0$ to q_t and rearranged to get

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (3.3)$$

The pseudo second order kinetics can be presented as

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (3.4)$$

The equation (3.3) then integrated for the conditions $t = 0$ to t and $q = 0$ to q_t and rearranged to get

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3.5)$$

or $$\frac{q_t}{t} = \frac{h}{1 + k_2 q_e t} \qquad (3.6)$$

where q_t, q_e are amount of surfactant adsorbed at time t and at equilibrium in μM g^{-1}, k_1 (min^{-1}), k_2 ($g\mu M^{-1}$ min^{-1}) are adsorption rate constants for pseudo–first–order and pseudo–second–order respectively. h ($\mu M g^{-1} min^{-1}$) can be regarded as the initial sorption rate as q_t/t, when t approaches 0. Hence,

$$h = k_2 q_e^2 \qquad (3.7)$$

The adsorption rate constants of both the models calculated by the above equations (3.3) and (3.5) as shown in Table 3.1. The high values of correlation coefficient (R_2^2) for the fitting obtained from the kinetic plots using the second model suggest that adsorption of surfactants on PTFE surface can be better expressed by the pseudo–second–order model as shown in Figure 3.3 (b). The results show the order of initial adsorption rates, TX-100>SDBS>CPB.

Table–3.1 Pseudo–first–order and pseudo–second–order kinetic parameters for SDBS, CPB, TX-100.

	Pseudo-first-order			Pseudo-second-order		
Surfactant	k_1 (min^{-1})	q_e ($\mu M.g^{-1}$)	R^2	k_2 ($g(\mu M.min)^{-1}$)	q_e($\mu M.g^{-1}$)	R^2
CPB	0.035	0.148	0.297	0.976	1.074	0.999
SDBS	0.064	0.084	0.140	0.811	1.102	0.998
TX–100	0.115	0.189	0.617	0.914	1.217	0.999

3.3.2 Adsorption isotherm

The adsorption isotherms of three surfactants on PTFE surface are represents in Figure 3.4. From the figure it is clear that the shapes of three different isotherms are not similar with different maximum amount adsorbed at saturation. The nature of the adsorption isotherm for TX-100 is apparently different, whereas, the other two ionics are close to similar. At lower surfactant concentration the change in amount adsorbed is not significant, whereas at higher concentration there is a significant change among the three surfactants. The order of equilibrium amount adsorbed at the plateau level is CPB > TX- 100 > SDBS.

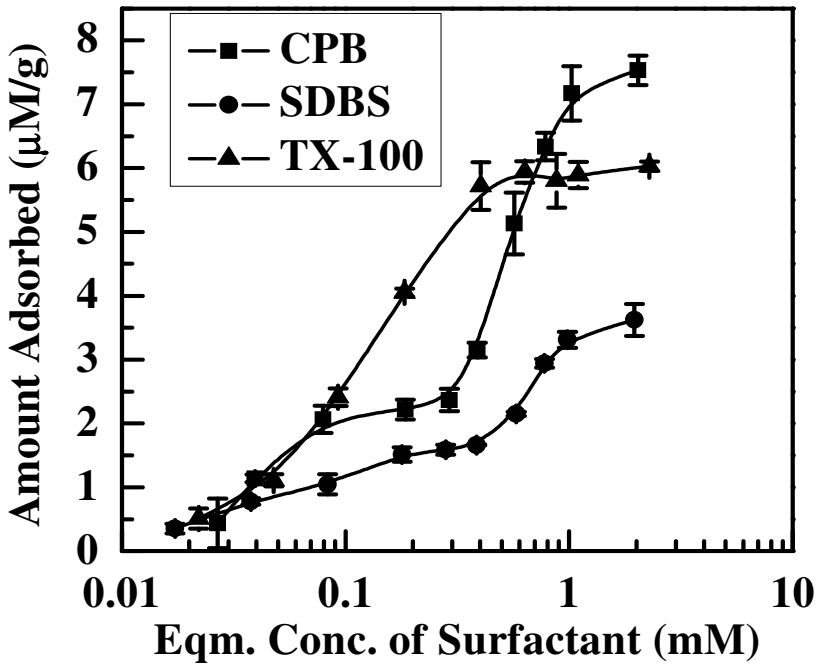


Figure 3.4 Adsorption isotherms of CPB, SDBS, and TX–100 on PTFE powder.

There are two types of models, Langmuir and Freundlich isotherms, generally used to correlate the amount adsorbed and the equilibrium concentration for the adsorption of surfactant molecules on a solid surface. The Langmuir and Freundlich isotherms may be expressed as the following equations:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{3.8}$$

$$\log q_e = \log a + \frac{1}{n}\log C_e \tag{3.9}$$

where q_m is equilibrium amount adsorbed (μM g^{-1}), b is the adsorption constant of Langmuir equation (mM^{-1}), C_e is the equilibrium concentration of surfactants in the solution (mM), a is a constant or coefficient of Freundlich isotherm equation representing the adsorption capacity, and n is a constant (reciprocal of the exponent of the Freundlich isotherm equation) depicting the adsorption intensity. When there is a negligible intermolecular interaction between the adsorbed surfactant molecules i.e., only monolayer of adsorbate is formed, the Langmuir model works quite well. In this study we have applied two models to test the better fitting of these isotherms. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients (R^2) are listed in Table 3.2.

Table 3.2 The parameters of Langmuir and Freundlich isotherm equations.

Surfactant	Langmuir			Freundlich		
	q_m ($\mu M.g^{-1}$)	$b \times 10^{-3}$ (mM^{-1})	R^2	a ($\mu M.g^{-1}$)	n	R^2
TX–100	6.622	0.301	0.990	6.382	1.879	0.848
CPB	10.101	0.18	0.895	6.309	1.647	0.914
SDBS	4.115	0.048	0.946	2.99	2.141	0.96
CPB+NaCl	10.638	0.462	0.971	8.260	2.469	0.939
CPB+Na_2SO_4	12.5	0.357	0.891	7.638	2.604	0.858
SDBS+NaCl	14.285	1.190	0.987	13.031	2.164	0.924

From Table 3.2, it is clear that TX-100 is following Langmuir isotherm with a R^2 value close to 1 and indicates a monolayer formation on the PTFE surface probably by adsorbing the tailgroup on the surface. Initially the adsorption density increases linearly with the equilibrium concentration, i.e., it follows Henry's law due to formation of monolayer, and ultimately reaches a plateau region at about 0.38 mM equilibrium concentration. Whereas for SDBS, both the models are almost equally fitted with an R^2 value above 0.94. For CPB there is a significant difference between the two isotherms with a higher R^2 value (~0.914) for Freundlich type. The ζ potential of PTFE particles show that the surface is having low negative charge, -4.82 mV, indicating it is mostly hydrophobic in nature, so we are expecting the majority of SDBS and CPB molecules also adsorb through the tailgroup. The shape of the isotherm indicates the sudden

change in adsorption amount is more sharp for CPB than SDBS and may be due to formation of hemimicelle. To support the higher hemimicellar aggregation number for CPB we have also calculated the hemimicellar aggregation number according to Gao et al. (1987) for both the surfactants and found the values are ~4 and ~2 for CPB and SDBS, respectively. So the aggregation of SDBS is not significant. In summary, we conclude SDBS isotherm follows mainly Langmuir type isothem and the similar fitting with Freundlich type model may be due to a small experimental error in the isotherm. The formation of hemimicelle on PTFE surface by the cationic surfactant (CTAB) is also reported by Dixit et al. (2002) and Vanjara and Dixtit, (1996) with an aggregation number 7. For the isotherms with hemimicelle formation at low surfactant concentration, amount adsorbed increases with the concentration and reaches an intermediate plateau reagion due to the saturation of monolayer, then with further increases in concentration there is a sudden rise in amount adsorbed due to the formation of hemimicelle. The critical concentration where hemimicelle formation occurs is called critical hemimicellar concentration (CHMC). In general, the driving force of hemimicelle formation is the hydrophobic interaction between the surfactant chains. At low concentration, however, the solution activity of the surfactant may not be sufficient to form any aggregation at the interface, thus the surfactants are still adsorbed as monomers. Above the CHMC the concentration of surfactants in solution is sufficient for formation of hemimicelle due to attraction of adsorbed molecule and the molecules present in the solution. The CHMC found from the isotherm is about 0.38 mM for CPB.The adsorption of three synthetic surfactants on PTFE surface may be predominated by hydrophobic interaction and there may be some other interactions such as electrostatic attraction, hydrogen bonding, and dispersion forces. There is a difference in amount adsorbed between these two ionic surfactants, having higher adsorption density for CPB. This may be attributed in terms of longer chain length of CPB than SDBS. In addition, as the surface is little negatively charged there will be repulsion between the SDBS molecules and the surface; whereas, there will be attraction between that of CPB and the solid surface. Ultimately, some CPB may also adsorb through the headgroup on the negatively charged sites and some on the hydrophobic sites through the tailgroup, finally they are also forming hemimicelle on the surface. These may be the reasons the adsorption of CPB is more than SDBS.

3.3.3 Effect of Electrolytes

3.3.3.1 Effect of Electrolytes on CMC

The solution property of surfactants also plays a major role in the adsorption behavior at the solid-liquid interface. Effects of three different salts NaCl, Na_2SO_4, and $CaCl_2$ on solution property and adsorption behavior of SDBS and CPB are studied here. Before studying the adsorption behavior in the presence of electrolytes we have studied the change in surface tension for a particular surfactant concentration with increasing electrolyte concentration as shown in Figure 3.5a and b.

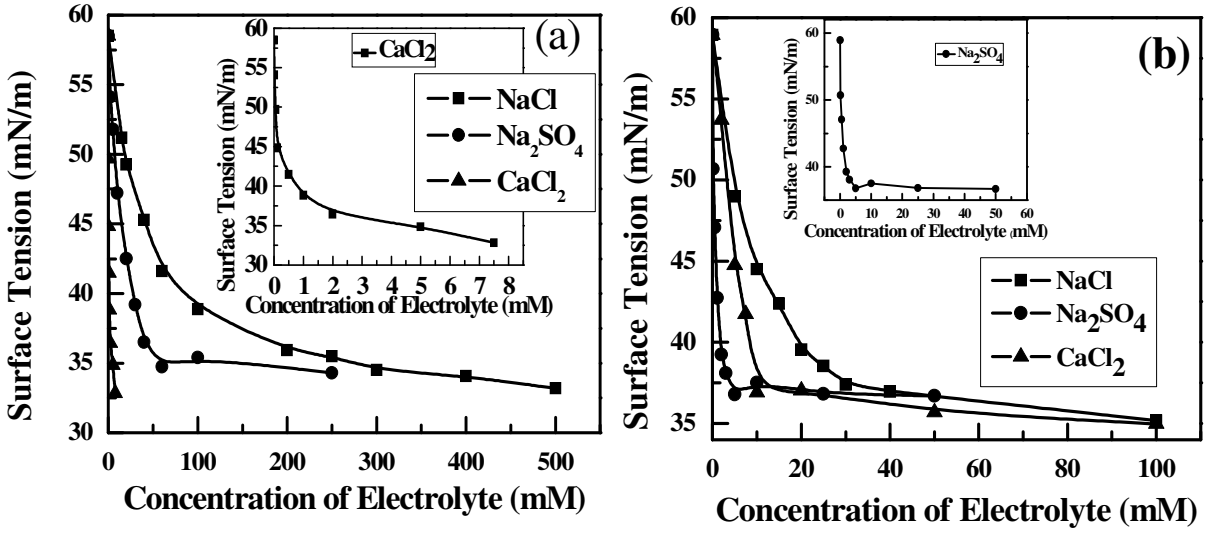


Figure 3.5: Surface tension reduction of surfactants solution in the presence of electrolytes. (a) SDBS, (b) CPB.

When the surface tension becomes constant we assume CMC is reached at that particular surfactant and electrolyte concentration. The CMCs of CPB and SDBS are 0.9 and 1.5 mM, respectively, in the absence of electrolytes. In the presence of electrolytes CMC was reached at concentration far below that of the original CMC, depending on the concentration of the electrolytes, as charge screening of the ionic surfactants headgroups and close packing of the surfactants occur at the air-liquid interface. Thus, inorganic salts have a significant impact on the adsorption of ionic surfactants at air-water as well as that in solid-water interfaces. According to the Schulze-Hardy rule, the charge screening efficiency or ability to reduce the debye length of a

multivalence ion is much more than a monovalence, so to get same CMC the required concentration of a multivalence salt required is significantly less than a monovalence. Table 3.3 shows the concentration of electrolytes required for getting CMCs of SDBS and CPB of 0.05 and 0.1 mM, respectively. SDBS and CPB have surface tension values at CMC in the absence of electrolytes 36.51 and 37.14 mN/m, respectively. The surface tension values of starting surfactant concentrations (0.05 mM and 0.1 mM) for SDBS and CPB are 58.50 and 58.97 mN/m, respectively. Table 3.3 shows surface tension values reached at CMC in the presence of electrolytes are very close to that of CMC in the absence of electrolytes. From the table it is clear that for CPB when the counterion is monovalence but co-ion is not monovalence a particular CMC value is reached when the ionic strengths (IS) of the electrolyte solutions are similar, for SDBS there is a little difference but it is close to the expected value (66 mM). In contrast, when the bivalence counterion is there for SDBS the concentration required is very close to that calculated according to Schulze-Hardy rule (according to this rule CaCl2 concentration required is $200/2^6$ = 3.12 mM). Whereas, CPB in the presence of bivalence counterion does not follow this rule, the concentration required is less than that of electrolyte having monovalence counterion but more than that according to Schulze-Hardy rule ($30/2^6$ = 0.468 mM).

Table 3.3 Concentration of electrolytes for reaching the CMC at a particular concentration of SDBS and CPB, and their surface tension (γ) values at initial concentration and at CMC.

Electrolytes	SDBS (0.05 mM)		CPB (0.1 mM)	
	Electrolyte conc. (IS)	γ (mN/m), initial value 58.50	Electrolyte conc. (IS)	γ (mN/m), initial value 58.92
NaCl	200 mM (IS = 200)	35.94	30 mM (IS = 30)	37.39
Na_2SO_4	60 mM (IS = 180)	35.26	5 mM (IS = 15)	36.79
$CaCl_2$	2 mM (IS = 6)	36.25	10 mM (IS = 30)	36.91

3.3.3.2 Electrolytes Effect on SDBS Adsorption at a Constant Concentration

Figure 3.6a and b shows the effect of electrolytes on adsorption of SDBS using a constant initial surfactant concentration at PTFE surface below and above the saturation. In this study a constant

surfactant concentration (0.05 mM) is used and the electrolytes concentrations are increased to see the change in adsorption. From Figure 3.6a, it is found that for all three electrolytes there is a linear increase in amount adsorbed with the increase in ionic strength of the electrolyte solution, with a correlation coefficient ~0.99 for all the three cases. First, we have done the adsorption study up to the electrolyte concentration where the CMC reached that particular surfactant concentration from the surface tension plot (Figure 3.5a, b), and found until that concentration there is no saturation in adsorption. This can be attributed as the initial concentration is constant in the presence of higher electrolyte concentration more surfactant molecules are getting adsorbed and ultimately the equilibrium concentration becomes still below the CMC at that electrolyte concentration, as a result, in this case we need to go to electrolyte concentration of far above than that shown in Table 3.3, to get the plateau. Figure 3.6b shows that with further increasing the concentration of electrolytes there indeed is a plateau level reached when the total surface of PTFE is covered. It is also worthy to observe that the maximum amount adsorbed at the plateau is very close for the three electrolytes, and that the amount is less than the plateau of the original adsorption isotherm in the absence of electrolytes above the CMC. It may also be interesting to note, at a constant surfactant concentration the effect of electrolytes show similar effect on amount adsorbed to that of increasing surfactant concentration, but in contrast, their nature of the curves are totally different. In the presence of electrolyte, there is a stiff linear rise in amount adsorbed until below the CMC then reached to a saturation level. From the linear fitting of the experimental data (ionic strength vs amount adsorbed) we found the increasing order of the slopes are Na_2SO_4 < NaCl , $CaCl_2$. In the presence of $CaCl_2$ the slope is 1 order of magnitude higher than those of the other two electrolytes. Quantitatively the slope in the presence of $CaCl_2$ is 35.87 times higher than that of Na_2SO_4 and 32.16 than NaCl. As we have mentioned before, since the surface is almost hydrophobic, adsorption may occur by the hydrophobic attraction between the tailgroup and the solid surface, in this situation reduction in headgroup repulsion or screening of headgroup charge in the presence of electrolyte is responsible for adsorption enhancement. The presence of bivalence counterion (Ca^{2+}) can effectively reduce the surface charge of the headgroup and show highest slope. Between NaCl and Na_2SO_4 bivalence co-ion has a negative effect on adsorption, so the slope is a little less in the presence of Na_2SO_4.

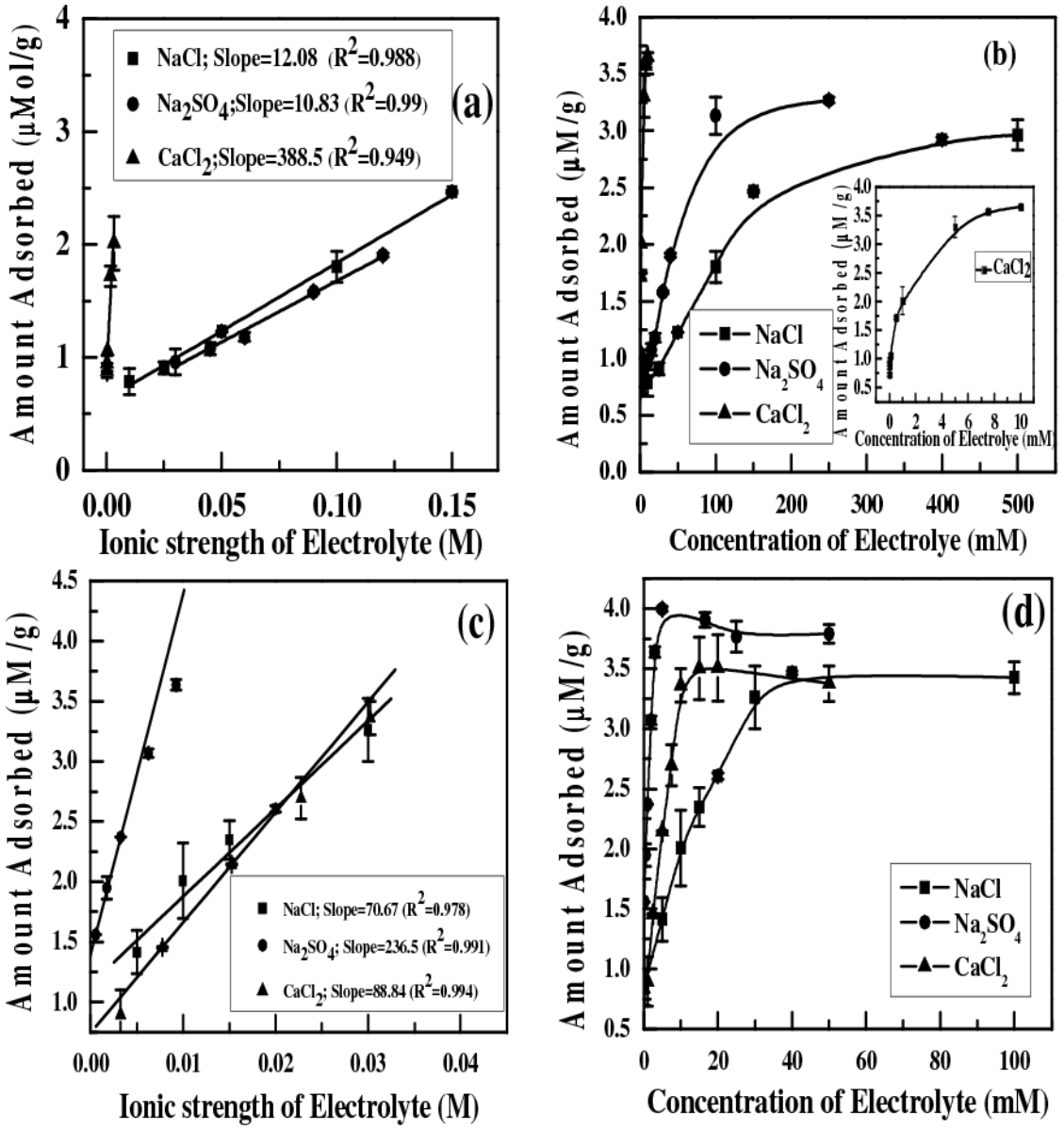


Figure 3.6(a) Linear increase of SDBS amount adsorbed with the increase in ionic strength of electrolyte solutions. (b) Plateau level of SDBS adsorption in the presence of different electrolytes solutions at higher concentration. (c) Linear increase of CPB amount adsorbed with the increase in ionic strength of electrolyte solutions. (d) Plateau level of CPB adsorption in the presence of different electrolytes solutions at higher concentration.

3.3.3.3 Electrolytes Effect on CPB Adsorption at a Constant Concentration

Figure 3.6c and d shows the adsorption behavior of CPB in the presence of electrolytes using a constant surfactant concentration below and above the saturation level, respectively. From the figure it can be seen that similar natures of the curves are obtained for CPB and SDBS. Figure 3.6c shows similar to SDBS there is a linear increase in the amount adsorbed with the increase in ionic strength of electrolytes solutions until below the CMC. The increasing orders of the slopes of the linear lines in the presence of electrolytes are NaCl < $CaCl_2$, Na_2SO_4. The slope in the presence of Na_2SO_4 is 2.65 times higher than that of $CaCl_2$ and 3.34 times than that of NaCl. So, similar to the previous study the rate of increase in adsorption is more when bivalence counterion is present than that of monovalence and less when bivalence co-ion is present. Comparing with the SDBS results we can also conclude the slope change is more sensitive to anionic surfactant and bivalence counterion combination rather than with cationic surfactant. The above results indicate the decrease in the electrostatic repulsion between the surfactant headgroups is the main mechanism here to increase the amount adsorbed due to closer packing at the surface. Figure 3.6d shows the amount adsorbed at the plateau is similar for NaCl and $CaCl_2$ and the difference is not significant from that in the presence of Na_2SO_4. Similar to anionic surfactants it can be seen that the maximum amount adsorbed is lower than that plateau of the isotherm in the absence of electrolyte. Since the amount adsorbed increases linearly and then reaches a plateau level, probably the monolayer formation is there in this surfactant concentration with a closer packing in the presence of electrolytes. In the earlier publication it was reported that during the adsorption of cationic surfactant in the presence of electrolytes on a hydrophilic surface the reduction in headgroup repulsion is important for adsorption enhancement (Paria and Yuet, 2006).

3.3.4 Area Occupied Per Molecule in the Presence of Electrolytes

Debye length (κ^{-1}) is defined as the inverse of the Debye–Huckel parameter, is the measure of screening of the electrical double layer in the presence of electrolyte. The Debye–Huckel parameter is represented as

$$\kappa = \left[\frac{1000 e^2 N_A}{\varepsilon_r \varepsilon_0 k_B T} \sum_i z_i^2 C_i \right]^{1/2} \qquad (3.10)$$

where e is the elementary charge, N_A is Avogadro's number, ε_r is the dielectric constant, ε_0 is the permittivity in vacuum, k_B is the Boltzmann constant, T is the absolute temperature, and z_i and C_i are the valence and molar concentration of ionic species i, respectively.

The Area per molecule is calculated as

$$A_{\min} = \frac{S \times 10^{26}}{\Gamma N_A} \tag{3.11}$$

where A_{min} is the area occupied per surfactant molecule in $Å^2$, S is the specific surface area of PTFE in m^2g^{-1}, and Γ is the amount of surfactant adsorbed at saturation in μMg^{-1}.

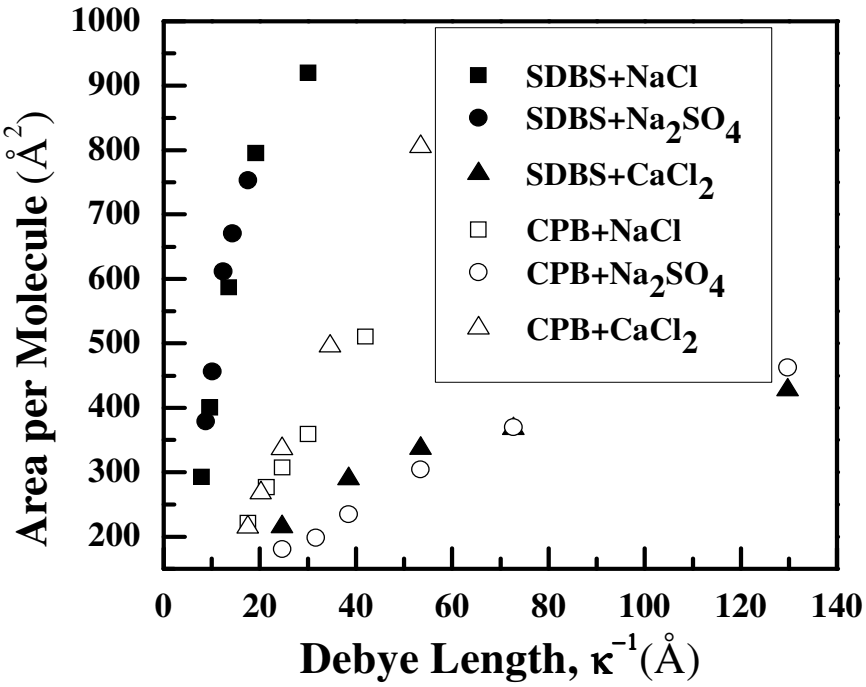


Figure 3.7 Area occupied per molecule of SDBS and CPB surfactants vs. Debye length ,κ^{-1} (Å). Areas occupied per molecule in absence of electrolyte are 996.40 $Å^2$ and 859.37 $Å^2$ for SDBS and CPB respectively.

From the Figure 3.7, it can be seen that the area occupied per SDBS molecule is linearly increases with the increase in Debye length. It is also found that the area occupied is very close for a particular Debye length in the presence of NaCl and Na_2SO_4 but different for $CaCl_2$, especially at higher Debye length. For a constant Debye length the area occupied per SDBS molecule is less in the presence of $CaCl_2$ than that of NaCl or Na_2SO_4. Figure 3.7, also shows a similar type of observation obtained for CPB. The area occupied per CPB molecule increases

linearly in the presence of electrolytes and almost similar with the variation of Debye length when the electrolytes are having mono–valance counter ion. In the presence of bi–valance counter ion (SO_4^{2-}) the area occupied per CPB molecule is less and the difference from the mono–valance counter ion is more at higher Debye length. This similar behavior for both the anionic and cationic surfactants is mainly due to the similar adsorption pattern of the molecules at the hydrophobic solid surface. Comparisons of both the surfactants together show there is a difference between the mono–valance counter ions for SDBS and CPB, but when bi–valance counter ion is present difference in area occupied by the two surfactants are almost similar.

3.3.5 Reduction in Surfactant Concentration

Since the amount adsorbed significantly increases in the presence of electrolyte, the reduction in surfactant concentration to obtained same amount adsorption was calculated and presented in Figure 3.8. For the calculation of % reduction, first the amount adsorbed for a particular initial concentration was taken from the adsorption isotherm data and the required electrolyte concentration to reach that amount adsorbed was calculated from the linear plot of amount adsorbed vs. ionic strength.

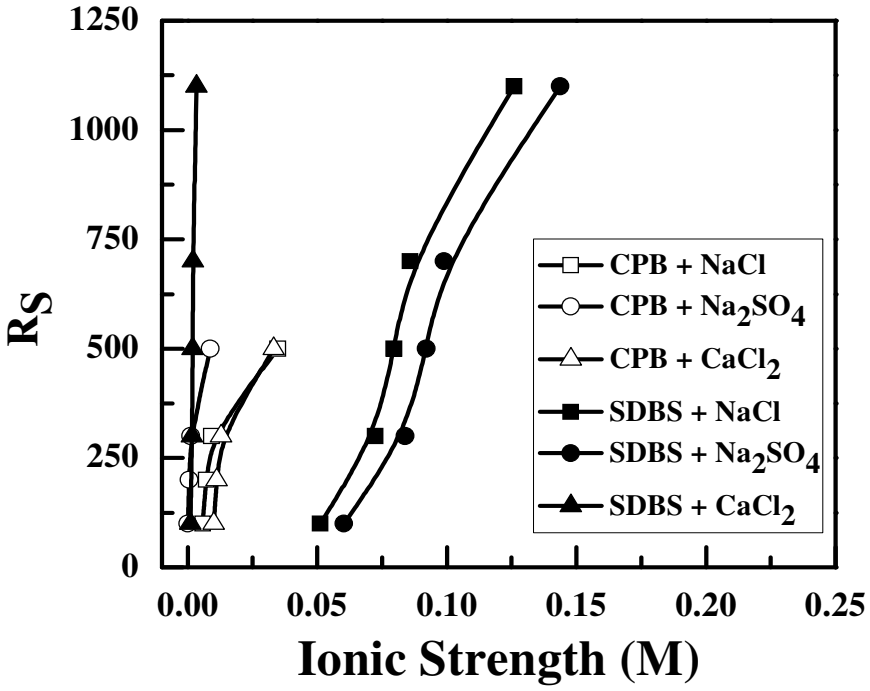


Figure 3.8 The reduction of surfactant consumption (R_S) with the increase in ionic strength of electrolyte solutions.

The % reduction of surfactant (R_S) was calculated according to the equation

$$R_S = \frac{(C_i - C_E)}{C_i} \times 100 \qquad (3.13)$$

where, C_i is the particular initial surfactant concentration from the isotherm, C_E is the concentration of surfactant used for study of electrolyte effect (0.05 mM for SDBS and 0.1 mM CPB). C_i was chosen in a particular range where the amount adsorbed fall in the linear range of Figures 3.6a and c. From the Figure 3.8 it can be seen that there is a significant increase in R_S with the increase in ionic strength and the reduction efficiency is more for SDBS systems, especially in the presence of $CaCl_2$.

3.3.6 Effect of Electrolytes on Surfactant Adsorption Isotherm

Figure 3.9, represents the adsorption isotherm of CPB in the presence of 50 mM NaCl, and 16.5 mM Na_2SO_4 each having equal ionic strength to study the counter ion valance effect on the isotherm. The isotherms are then fitted with Langmuir and Freundlich model and the parameters are listed in Table 3.2.

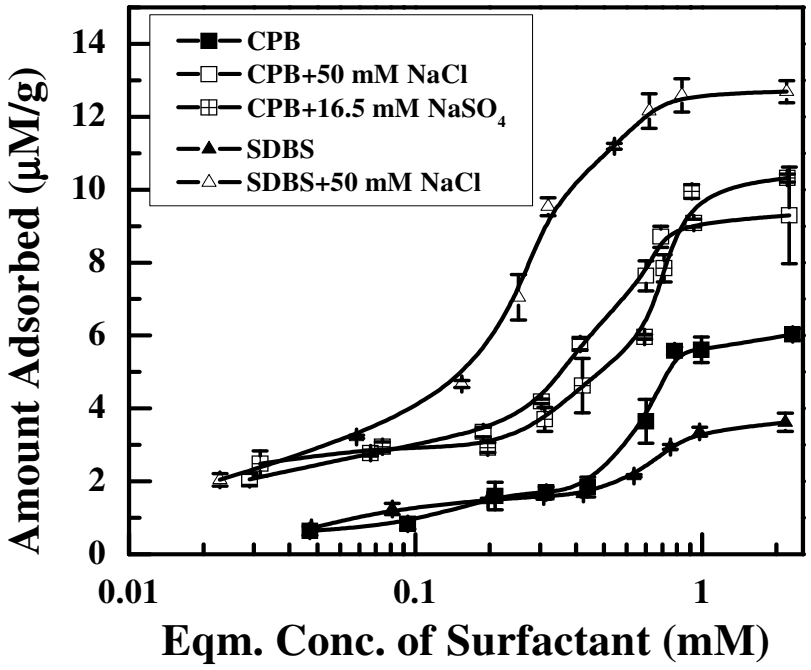


Figure 3.9 Adsorption isotherms of CPB, CPB + 50 mM NaCl, CPB + 16.5 mM Na_2SO_4, SDBS, SDBS + 50 mM NaCl on PTFE powder.

From the Table it is observed that for both the cases Langmuir isotherm fits better than Freundlich isotherm. In the presence of electrolytes the negative surface charge of PTFE surface

may be reduced further, as a result the surfactants are mostly adsorbing like a uniform hydrophobic surface. That may be the reason why the isotherm is shifted from Freundlich to Langmuir type. The increase in amount adsorbed in plateau region is due to mainly reduction in headgroup repulsion that explained before. Higher adsorption amount in the presence of Na_2SO_4 shows counter ion valance effect is more important although the ionic strength is same. Throughout the isotherm since the ionic strength is constant the difference in amount adsorbed between NaCl and Na_2SO_4 is less.

Figure 3.9, also depicts the adsorption isotherm of SDBS without electrolyte and at 50 mM NaCl. For SDBS we have not studied the effect of $CaCl_2$ due to formation precipitate at 16.5 mM concentration. Similar to CPB adsorption isotherm of SDBS also shows better fitting with Langmuir model may be due to similar reason. The amount adsorb increased also due to further decrease in surface potential and also reduction in headgroup repulsion between the adsorbed molecules. The adsorption of pure surfactants show CPB is having higher adsorption capacity than SDBS, whereas, in the presence of NaCl the trend is reverse. This observation can be attributed in the following ways: (i) in the presence of NaCl for CPB when the surface charge is reduced, the number of molecules adsorbed due to oppositely charged surface is reduced, and the adsorption enhancement is only due to the reduction in headgroup repulsion. (ii) For SDBS adsorption, the repulsion between same charged surface and headgroup is reduced, which is favorable for adsorption in addtion to reduction in headgroup repulsion. As a result, SDBS shows higher adsorption capacity at the plateau level in the presence of NaCl than that of CPB.

3.4 Conclusions

The rate of adsorption of three synthetic surfactants TX–100, SDBS, and CPB on PTFE surface is very fast; within 10 minutes the equilibrium is reached. Pseudo–second–order kinetic model fits well for the adsorption kinetics of all three surfactants with the following order of rate constant values with a minimum difference: CPB > TX–100 > SDBS. The adsorption isotherms of TX–100 show Langmuir type but SDBS and CPB are better fit with Freundlich type model. In the presence of electrolytes, isotherms of both the ionic surfactants show better fitting with Langmuir type isotherm. When the initial concentration of the ionic surfactant is constant and far below the CMC, the addition of electrolytes show there is a linear relationship between the amount of surfactant adsorbed and ionic strength of the electrolyte solutions. The increasing

order of the slopes in the linear portion for SDBS is: Na_2SO_4 < NaCl << $CaCl_2$ and that for CPB: NaCl < $CaCl_2$ << Na_2SO_4. The area occupied per molecule (A_m) also changes linearly with the Debye length in the presence of electrolytes for both the ionic surfactants. The A_m is mainly dependent on Debye length but independent on the types of electrolytes when mono–valance counter ion is present. Whereas, in the presence bi–valance counter ion for a particular Debye length the difference in A_m is observed. The difference in A_m in the presence of mono– and bi–valance counter ion is more at higher Debye length. The main mechanism of increase in amount adsorbed for both the surfactants can be attributed to the decrease in the electrostatic repulsion between the surfactant headgroups, as a result, closer packing of the surfactant molecules at the surface.

This study gives an idea about the adsorption behavior of anionic and cationic surfactants on a hydrophobic surface in the presence of electrolytes. The study may be useful in some applications like wetting, colloid stability, dispersion of polymers etc. where surfactant adsorption is an important parameter; moreover, surfactant consumption can also be reduced by adding small amount of electrolytes to the surfactant solutions.

Chapter-4

Wetting behavior of TX-100 and Igepal CO 630 on PTFE surface.

Chapter-4

Wetting behavior of TX-100 and Igepal CO 630 on PTFE surface

4.1 Introduction

The wetting of hydrophobic surfaces by surfactant solutions is very important in surface and interface science, owing to the fact that many industrial processes and daily life applications are impossible to consider without wetting. In the wetting process, adsorption of surfactant at the solid-liquid interface and surface tension at the air-liquid interface plays an important role. Because hydrophobic surfaces have very low surface energies, wetting with a polar solvent is difficult and can be enhanced using surfactants. Surfactants having low surface tension values at the critical micellar concentration (CMC) and low solid-water interfacial tension upon the adsorption of surfactants always show better wetting properties.

In view of the widespread applications of wetting phenomena, many researchers have studied the wettability of different types of hydrophilic and hydrophobic surfaces by different single surfactants (Zhang et al., 2010; Scales et al., 1986), mixed surfactant systems (Szymczyk, et al., 2006; Szymczyk and Janczuk, 2006; Szymczyk and Janczuk, 2007), and additives (Zdziennicka et al., 2005; Chaudhuri and Paria, 2009). In mixed surfactant systems, mixtures of similar cationics (Szymczyk, et al., 2006), and nonionics (Szymczyk and Janczuk, 2007), and dissimilar mixtures of both cationic and nonionic surfactants (Bogdanova et al. 2003; Szymczyk and Janczuk, 2006), have been studied. The effects of different additives such as alcohols (Zdziennicka et al., 2005; Zdziennicka and Janczuk, 2008a, b; Zdziennicka, 2008, 2009), and electrolytes (Chaudhuri and Paria, 2009) have also been studied thoroughly.

In general, nonionic surfactants are preferable in many applications because of their biocompatibility, lower sensitivity toward electrolytes, low CMC and surface tension values compare to those of ionics, and so on. For a long time, many researchers have studied the wetting behaviors of nonionic surfactants on both hydrophilic and hydrophobic surfaces for different applications (Scales et al., 1986; Chander et al. 1987; Gau and Zografi, 1990; Kim and Hsies, 2001; Mohammadi et al., 2004; Halverson et al., 2009; Radulovic et al., 2009a; Zdziennicka et al., 2009). Mostly, the wetting properties increase in the presence of nonionic surfactants for both hydrophilic and hydrophobic surfaces. The wetting properties also depend on the molecular structure of the surfactant (Simoncic et al., 2007), as well as the nature of hydrophilic and hydrophobic groups of different surfactants. The wetting properties of a nonionic surfactant can

also be improved using alcohols of different chain lengths (Zdziennicka, 2010), binary mixtures (Szymczyk and Janczuk, 2006; Szymczyk and Janczuk, 2007; Hu et al. 2000; Szymczyk and Janczuk, 2008), and ternary surfactant mixtures (two nonionic + one ionic) (Szymczyk and Janczuk, 2010).

The present study focuses on the adsorption and wetting behaviors of two nonionic surfactants (TX-100 and Igepal CO- 630) having similar head groups but dissimilar tail groups on a polytetrafluoroethylene (PTFE) surface. The surfactants have similar head groups, nine ethylene oxide groups attached to a benzene ring, but a structural difference in the tail groups. Igepal CO-630 and TX-100 contain n-nonyl (C_9) and an eight-carbon branched chain (C_8) hydrocarbon (1,1,3,3-tetramethylbutyl), respectively, as the tail group. The adsorption behaviors of the surfactants between the PTFE-water and air-water interfaces obtained from the wetting study were also compared with the results of independent adsorption studies at those respective interfaces. To the best of our knowledge, this type of study has not been reported before. TX-100 and Igepal CO-630 were chosen because they are members of the typical alkyl polyethylene oxide category widely used in several practical applications. Moreover, from the environmental viewpoint, straight-chain hydrophobic groups are more important because of their biodegradable nature than branched chains in a nonionic surfactant.

4.2 Materials and Methods

4.2.1 Materials

Polytetrafluoroethylene (PTFE) slide of dimension 25.34 mm × 1.12 mm was cut from a sheet purchased from J. Khushal Das and Co., Mumbai, India and the microscopic glass slides 25.02 mm × 1.26 mm were purchased from Blue Star, India. Triton X–100 (TX–100) (*p*-(1,1,3,3-tetramethylbutyl) phenoxypoly ethylene glycol), Igepal CO 630 (polyoxyethylene nonyl phenol), were purchased from Sigma–Aldrich chemicals, Germany (Technical grade, Cat no. 93418, and 542334 respectively) and used without any further purification are shown in Figure 4.1.

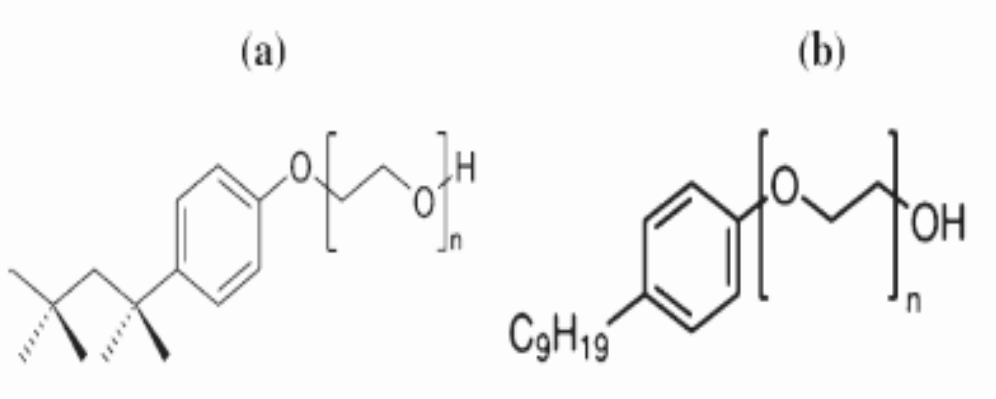


Figure 4.1: Structures of the surfactant molecules: (a) TX-100, (b) Igepal CO 630.

4.2.2 Methods

4.2.2.1 Surfactant Adsorption Isotherm and Kinetics on a PTFE Surface

The surfactants adsorption kinetics and isotherm of on PTFE powder were measured according to the method described in section 3.2.2.2.

4.2.2.2 Measurement of Surface Tension and CMC

The surface tension and CMC of the surfactants were measured according to the method described in section 3.2.2.1.

4.2.2.3 Measurement of Contact Angle

Dynamic advancing (θ_A) contact angle was measured by Wilhelmy balance method using the above mentioned surface tensiometer. All the experiments were carried out at constant temperature (25 ± 0.5 ℃). Motor speed of 0.2 mm/sec and immersion depth of the PTFE plate 5 mm was maintained during the contact angle measurements. A good quality PTFE plate was chosen and washed several times with first acetone and then ultrapure water to clean the impurity. The plate was then dried by blowing hot air. The same procedure was repeated after the measurement of each surfactant concentration.

4.3 Results and Discussion

4.3.1 Surfactant Adsorption Isotherm on PTFE Surface

The adsorption isotherm was also determined to see the difference in amounts adsorbed at equilibrium in a range of concentrations from below to above the CMC for both surfactants. Figure 4.2 presents the adsorption isotherms of the two nonionic surfactants on a PTFE surface. Because of the chemical inertness of the low-energy hydrophobic solid surface, chemical interaction with the surfactant is minimal. From the figure, it is clear that the natures of the adsorption isotherms for TX-100 and Igepal CO-630 are similar and are of Langmuir type.

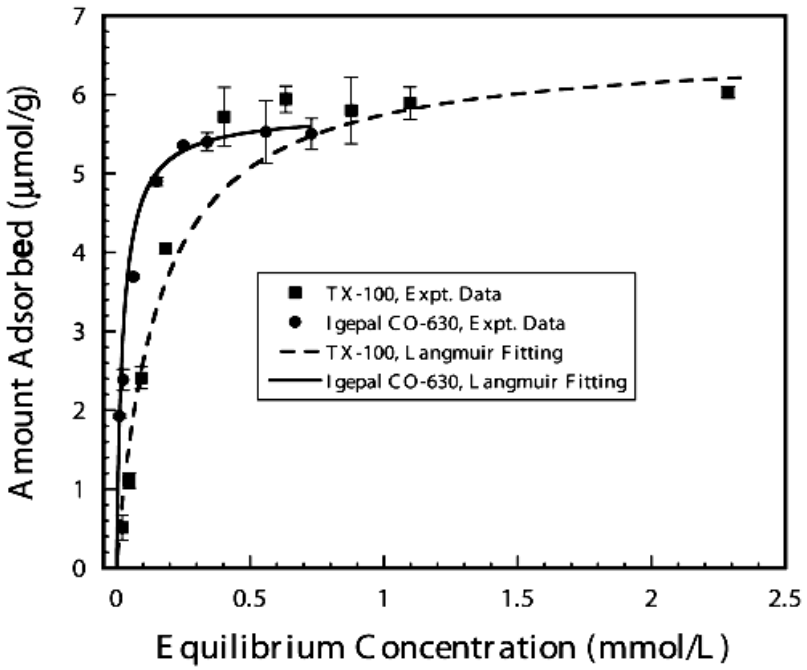


Figure 4.2 Adsorption isotherms of TX-100 and Igepal CO-630 on PTFE powder.

Initially, at low equilibrium concentration, because of the presence of more free accessible sites, the isotherm rises linearly with a higher slope, whereas at higher equilibrium concentration, the formation of a plateau region indicates monolayer coverage of the surfactants on the PTFE surface because of the negligible intermolecular interaction between the adsorbed surfactant molecules. Comparison between the two isotherms shows that, at low surfactant concentrations, the amount adsorbed for Igepal CO-630 is higher than that for TX-100, which might be due to the bulkiness of the TX-100 molecule. In contrast, at the plateau level, TX-100 has a slightly higher amount adsorbed, although the change is not very significant. Both isotherms were fitted with the Langmuir and Freundlich models, and better fits were found with the Langmuir model. The linear forms of the Langmuir and Freundlich isotherms are given by equation (3.8) and (3.9) of the previous chapter. Values for the parameters are listed in Table 4.1

Table–4.1 Parameters of the Langmuir and Freundlich Isotherm Models

Surfactant	Langmuir			Freundlich		
	q_m (µM g^{-1})	b(µM^{-1})	R^2	a (µM g^{-1})	n	R^2
TX–100	6.62	0.30	0.99	6.38	1.87	0.84
Igepal - 630	5.78	43.25	0.99	6.99	3.70	0.92

4.3.2 Surfactant Adsorption Kinetics on PTFE Surface

Because adsorption is inherently associated with the wetting process, the adsorption kinetics was studied to determine the equilibrium time, as well as the rates of adsorption of the two different nonionic surfactants (TX-100 and Igepal CO-630) from a solution with an initial concentration of 0.05 mM on a PTFE surface in a batch study. The data on the kinetics of adsorption are shown in Figure 4.3, from which it is clear that the rate of adsorption is very high for both surfactants, with equilibrium times of approximately 10 min for TX-100 and 5 min for Igepal CO-630 and a higher adsorption amount for Igepal CO-630.

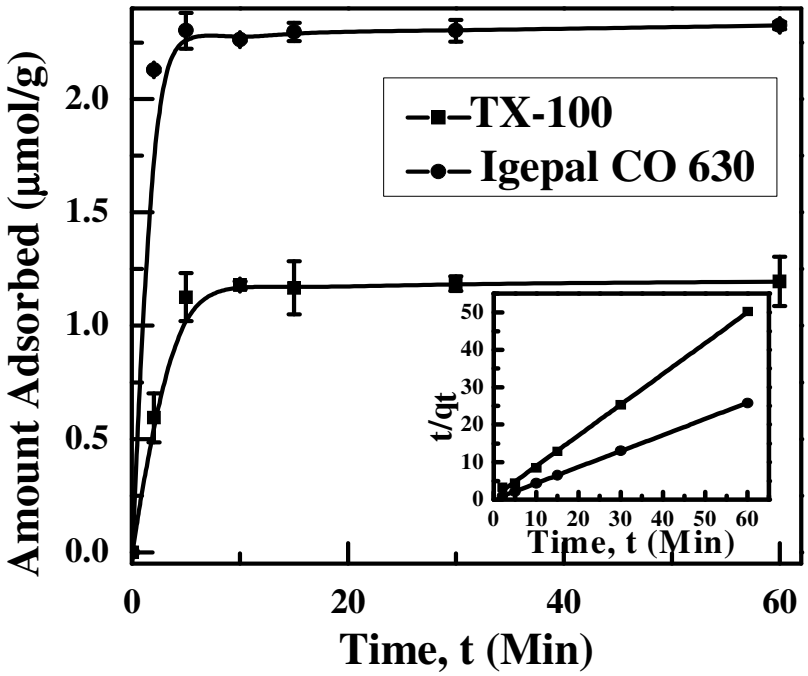


Figure 4.3 Adsorption kinetics of TX-100 and Igepal CO-630 on PTFE powder. Inset shows linear fitting of pseudo-second-order kinetics.

As the surface is mostly hydrophobic, adsorption of these nonionic surfactants occurs by attachment of the tail group through van der Waals forces. Now, to calculate the rate constant of the process, the experimental results were fitted with pseudo-first-order and pseudo-second-order models, and better fits were found for the second-order model using the linear form of the equations (3.3) and (3.5) of the previous chapter. The adsorption rate constants of both models calculated by those equations are reported in Table 4.2.

For both surfactants, the correlation coefficient for fitting (R^2) was found to be close to 1, with second-order adsorption rate constants of 0.91 and 2.09 g (μM min)$^{-1}$ for TX-100 and Igepal

CO-630, respectively. The high R^2 values obtained from the kinetic plots suggest that adsorption of surfactants on a PTFE surface can be better expressed by the pseudo-second-order model, as shown in Figure 4.3, having a higher R^2 value (>0.99) than the pseudo-first order model. From the data, it is clear that, at a constant surfactant concentration, the rate of adsorption is higher for Igepal CO-630 than for TX-100, which might be due to the presence of a straight chain hydrophobic tail group in Igepal CO-630.

Table 4.2 Pseudo-First-Order and Pseudo-Second-Order Kinetic Parameters

Surfactant	Pseudo first order kinetics			Pseudo second order kinetics		
	k_1 (min^{-1})	q_e (μmol/g)	R^2	k_2 (g.(μmol·min)$^{-1}$)	q_e (μmol/g)	R^2
TX-100	0.11	0.19	0.61	0.91	1.21	0.99
Igepal-630	0.04	0.08	0.35	2.09	2.33	1

4.3.3 Area Occupied Per Surfactant Molecule at PTFE–Water Interface

From the maximum adsorption capacity, the molecular density or the adsorption density of the surfactants can be expressed in terms of the effective area occupied per surfactant molecule at the PTFE-water interface. Assuming that monolayer adsorption occurs at the PTFE-water interface area, the occupied per molecule can be calculated as (Rosen, 2004)

$$A_{\min} = \frac{1}{N_A \times \Gamma_{SL}} \tag{4.5}$$

$$\Gamma_{SL} = \frac{q_m}{S_{BET} \times 10^6} \tag{4.6}$$

where A_{min} is area occupied per molecule (nm^2), Γ_{SL} is the surface excess concentration of surfactant (mM/m^2) at the PTFE-water interface, q_m is the amount of surfactant adsorbed on the PTFE surface (μM/g) calculated from the Langmuir adsorption isotherm equation, S_{BET} is the BET surface area of the PTFE powder (m^2/g), and N_A is Avogadro's number (6.02×10^{23}). The values for the area occupied per molecule obtained from the above equations for TX-100 and Igepal CO-630 are 1.09 and 1.24 nm^2, respectively.

4.3.4 Change in Contact Angle with the Surfactant Concentration

The change in advancing contact angle on the PTFE surface was studied and is plotted in Figure 4.4. Figure 4.4 shows that there is a gradual decrease in contact angle with increasing surfactant concentration until 0.1 mM (log c = -1) for Igepal CO-630 and 0.3 mM (log c = -0.5) for TX-100; beyond that concentration, the contact angle remains constant. The contact angle changes from 117.14º (pure water) to 80.42º with increasing concentration of TX-100; similarly, for Igepal CO-630, the change is from 117.14º to 82.79º.

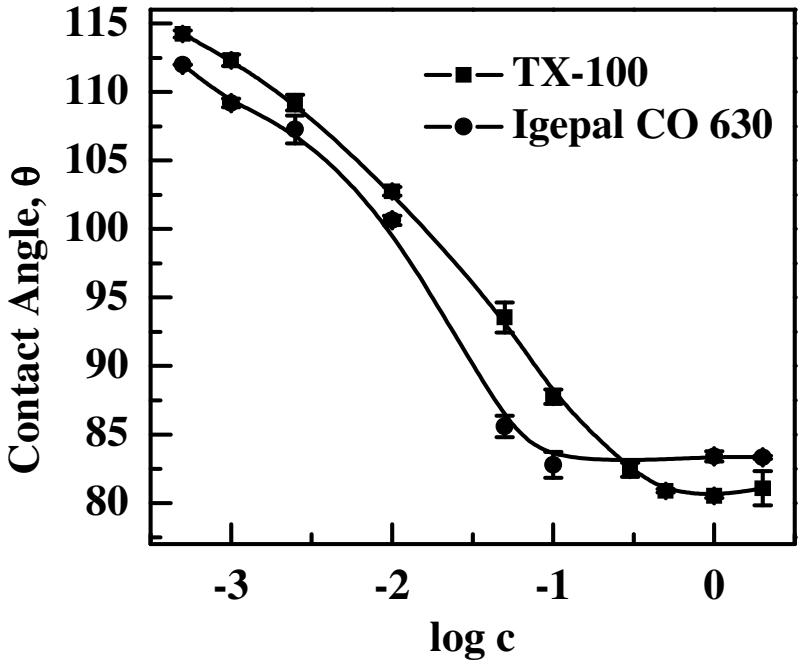


Figure 4.4 Change in contact angle (θ) with concentration (log c) for different surfactants.

Thus, for both surfactants, the contact angle decreases until close to the CMC. The contact angles are similar for the two surfactants, with a slightly lower value for Igepal CO-630 below the CMC region, although the final saturation value is ~2º lower for TX-100. Comparison of these plots with the adsorption isotherm reveals some similarities, such as that the amount of Igepal CO-630 adsorbed is also higher at low concentration and that, near the CMC, TX-100 shows a slightly higher adsorption value at the plateau level, although the difference is not significant. This result can be explained as being due to a close relationship between the decrease in contact angle on the PTFE surface and the adsorption density. As mentioned before, this behavior might be due to

the presence of the straight-chain tail in Igepal CO-630 resulting in a higher adsorption density at lower concentration as well as a greater lowering of the contact angle.

4.3.5 Surface Excess at PTFE–Water and Air-Water Interfaces

Similarly to the adsorption of surfactants at the solid-liquid interface, that at the air-liquid interface is also important in the wetting process. Adsorption of a surfactant at a solid-liquid interface contributes to the wetting process by changing the hydrohilicity/hydrophobicity or the surface energy.

Likewise, adsorption of a surfactant at an air-liquid interface changes the surface tension, which is similar to the surface energy at the air-liquid interface. The contact angle can be related to the surface or interfacial tensions using Young's equation as

$$\gamma_{LG} \cos\theta = \gamma_{SG} - \gamma_{SL} \tag{4.7}$$

where γ_{SL}, γ_{LG}, and γ_{SG} are the interfacial tensions between the solid–liquid, air-liquid, and solid–gas interfaces respectively. The amount adsorbed or surface excess (Γ_{LG}) at air-liquid interface in mol/m^2 can be calculated as

$$\Gamma_{LG} = -\frac{1}{2.303RT}\frac{d\gamma_{LG}}{d\log C} \tag{4.8}$$

where R is the universal gas constant (8314 m^3 Pa/kg mol K), T is absolute temperature, and N_A is Avogadro number (6.02×10^{23}). Similarly, surface excess in other two interfaces (Γ_{SG} and Γ_{SL}) can also be calculated. Rearranging the surface excess equations for three interfaces, and substituting equation (4.7) gives Lucassen–Reynolds equation (Lucassen-Reynders, 1963, 1965).

$$\frac{\Gamma_{SG} - \Gamma_{SL}}{\Gamma_{LG}} = \frac{d(\gamma_{SG} - \gamma_{SL})}{d\gamma_{LG}} = \frac{d\gamma_{LG}\cos\theta}{d\gamma_{LG}} \tag{4.9}$$

The surface excess at the solid-gas interface can be assumed to be zero ($\Gamma_{SG} \approx 0$). The ratio of Γ_{SL} to Γ_{LG} can be obtained from the slope of a plot of $\gamma_{LG} \cos\theta$ (adhesional tension) versus γ_{LG}. If the slope of the curve (Γ_{SL}/Γ_{LG}) is -1, then the surface excesses at the solid-liquid and air-liquid interfaces are equal. The plot of adhesional tension versus surface tension shows a linear relationship with a slope of -0.86 ($R^2 = 0.98$) shown in Figure 4.5. It was also found that there was no difference between the two surfactants. This indicates that the surface excesses at the PTFE-water and air-water interfaces are not equal. To calculate the actual surface excess at the air-water interface, the surface tension of each surfactant solution was measured, and eq 4.5 was

used to calculate the values A_{min}. The surface excess values obtained from the experimental data are also comparable with the previously reported values included in Table 4.3. This table shows that the values of surface excess are similar for the two surfactants. The ratios of the surface excess values between two interfaces are 0.65 and 0.58 for TX-100 and Igepal CO-630, respectively, which also confirms the inequality in surface excess at the two interfaces, in agreement with the contact angle results.

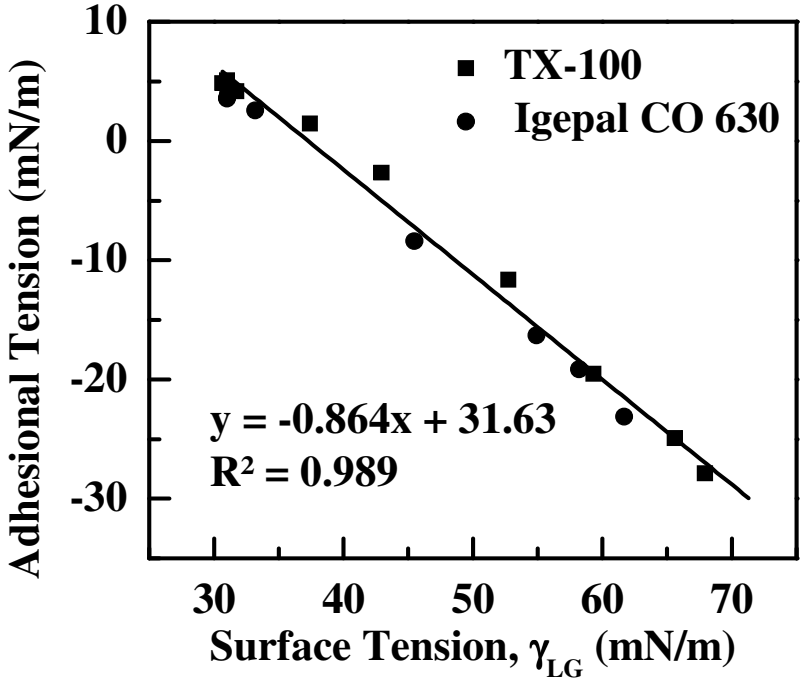


Figure 4.5 The plot of surface tension (mN/m) vs. adhesional tension (mN/m) of different surfactants.

The values show that there is a little difference in the Γ_{SL}/Γ_{LG} ratio between the two surfactants measured independently and that these values are lower than those obtained from the contact angle measurements. This difference can be attributed to the following causes: (i) There are differences between the different measurement techniques. (ii) The PTFE sheet and powder were obtained from different sources, which could result in variations in quality. (iii) The amounts of surfactant adsorbed on the PTFE surface are low, and the UV-vis measurement technique is not very precise, so that some experimental error could also be incurred in the adsorption experiments. For the confirmation of equal adsorption at the solid-liquid and air-liquid interfaces, $\Gamma_{SL}/\Gamma_{LG} = -1$ is a necessary condition. At the same time, another condition should also be fulfilled: linearity of the plot of cos θ versus $1/\gamma_{LG}$ with an intercept on the cos θ axis equal to -1.

The plot of our results as shown in Figure 4.6 indicates that there is a linear relationship between cos θ and $1/\gamma_{LG}$ with an intercept of -0.84 ($R^2 = 0.98$).

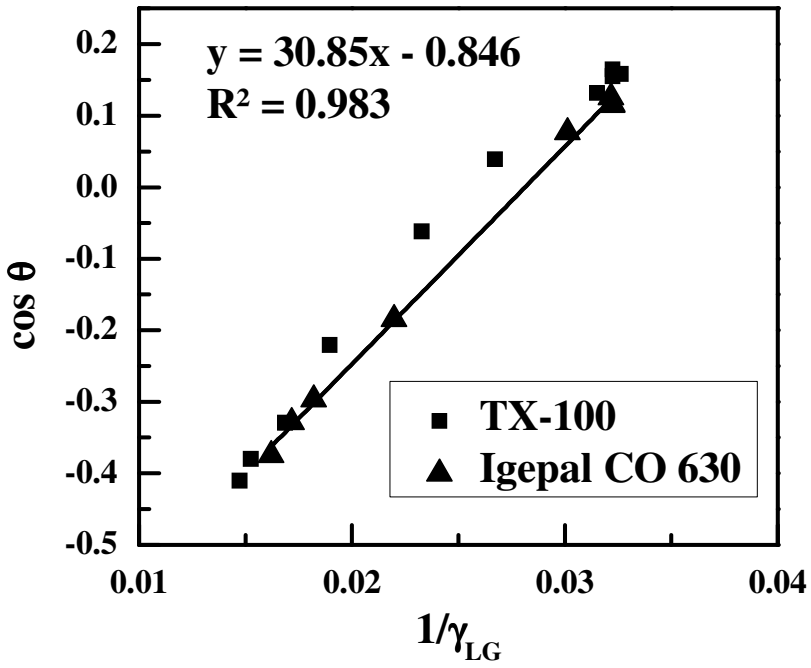


Figure 4.6 The plot of cos θ vs. inverse of surface tension of different surfactants.

Finally, it can be concluded that the surface excess concentrations at the PTFE-water and air-water interfaces are not equal in this study. In this regard, there is no general rule for predicting whether the surface excesses at the solid-liquid and air-liquid interfaces will be equal; rather, it might depend on the solid surface as well as the type of surfactant. From some previously reported studies, it appears that, for low-surface-energy solids, the surface excesses at the solid-water and air-water interfaces are same (Szymczyk, et al., 2006; Zdziennicka and Janczuk, 2008b; Zdziennicka, 2008; Bargeman and Vader, 1973); however, other studies have also reported unequal adsorption between hydrophobic solid-water and air-water interfaces, such as nylon and poly(methyl methacrylate) (PMMA) (Szymczyk, et al., 2006; Pyter et al., 1982) and PTFE (Chaudhuri and Paria, 2009).

Table 4.3 CMC, surface tension at CMC, surface excess at air-liquid interface, and area occupied per molecule for TX-100 and Igepal CO 630.

Surfactant	CMC (mM)	γ_{CMC} (mN/m)	Exp Γ_{LG} (mol/m^2) x 10^6	Exp A_{min} (nm^2)	Literature Γ_{LG} (mol/m^2) x 10^6	Literature A_{min} (nm^2)
TX-100	0.15	31.01	2.36	0.70	2.5 (at 25 ºC)[a]	0.66[a]
Igepal CO 630	0.08	31.02	2.31	0.71	3.25[b]	0.51[b]

[a] (Rosen, 2004), [b] (Bielska et al., 2005)

4.3.6 PTFE–Water Interfacial Tension and Critical Surface Tension of Wetting

From equation (4.7), it is clear that the PTFE-water interfacial tension is also equally important in the wetting process as the air-water interfacial tension or surface tension. For reducing the contact angle at the PTFE-water interface, reductions in both interfacial tensions are essential.

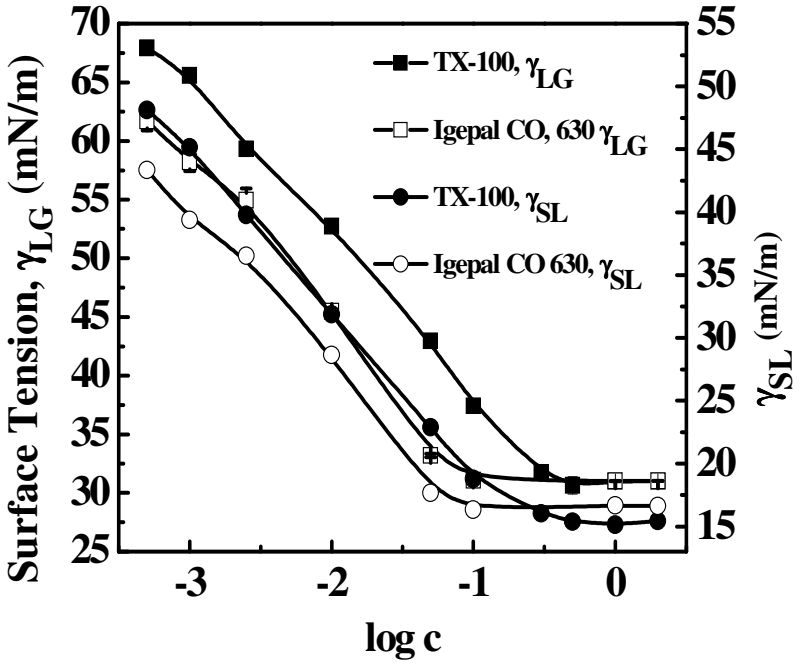


Figure 4.7 Change in surface tension (mN/m) and PTFE_water interfacial tension with the surfactant concentration (log c).

Figure 4.7 shows the changes in both the interfacial tensions with log c. From the figure, it is clear that Igepal CO-630 has a slightly lower value for both the interfacial tensions than TX-100, whereas their plateau levels are almost same. The PTFE-water interfacial tension changes from 52.85 mN/m(pure water) to 15.43 and 16.36 mN/m for TX-100 and Igepal CO-630, respectively,

and the surface tension value changes from 71.50 mN/m (pure water) to 31.01 and 31.02 mN/m for TX-100 and Igepal CO-630, respectively. As in previously reported studies (Bernett and Zisman, 1959a,b), there is a linear relationship between cos θ and γ_{LG}, as shown in Figure 4.8. The critical surface tension (γ_C) value of 23.62 mN/m was obtained by extrapolating the curve to cos θ = 1; this value is close (23.46 mN/m) to that reported before (Szymczyk and Janczuk, 2007).

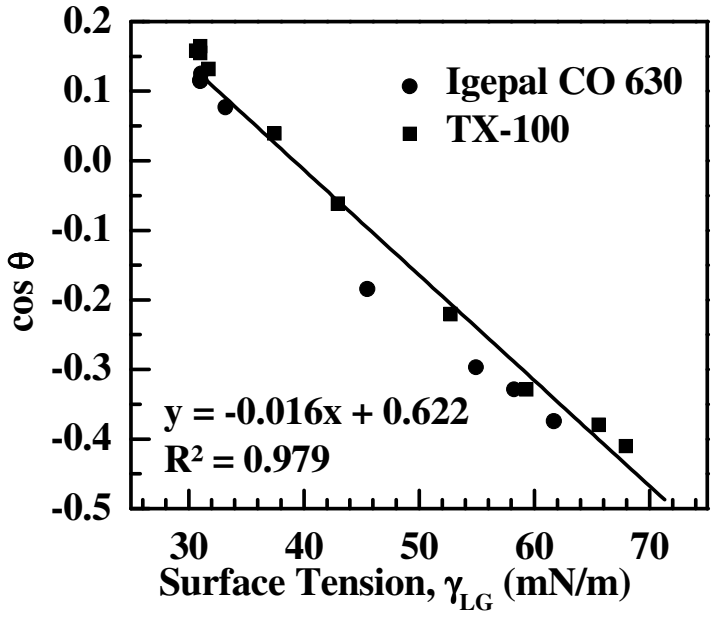


Figure 4.8. Plot of cos θ versus surface tension (mN/m) for different surfactants.

4.3.7 Work of Adhesion of Surfactant Solutions to PTFE Surface

The work of adhesion measures the interactive force between the two different (solid and liquid) phases. The interaction between the two phases and the contact angle can be presented using the Dupree and Young- Dupree equations, respectively

$$W_A = \gamma_{LG} + \gamma_{LG} - \gamma_{SL} \tag{4.10}$$

$$W_A = \gamma_{LG}(1 + \cos\theta) \tag{4.11}$$

The work of adhesion depends on both surface tension and contact angle; for zero contact angle, $W_A = 2\gamma_{LG}$. Therefore, zero contact angle results when the forces of attraction between liquid and

solid are equal to or greater than those between liquid and liquid, and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself. The values of the work of adhesion at different surfactant concentrations are plotted in Figure 4.9. This figure shows that the values of W_A decrease with a slight irregularity with increasing concentration of surfactant. Igepal CO-630 has lower W_A values than TX-100. The change in W_A with surfactant concentration can also be attributed to the unequal surface excesses between the air–liquid and solid_liquid interfaces. Mathematically, this can be shown as follows. The differential form of equation (4.11) can be written as

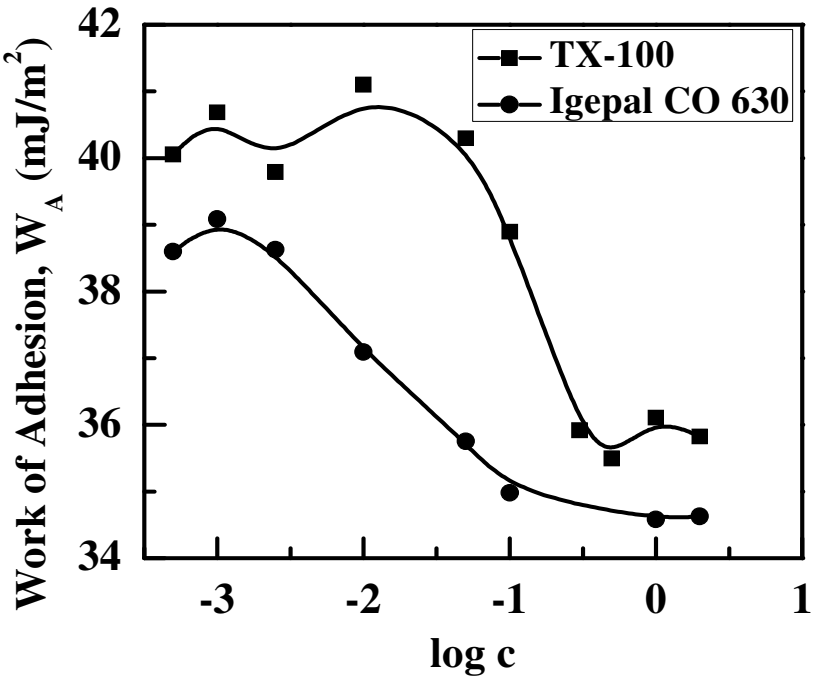


Figure 4.9 Change in the work of adhesion (W_A) with surfactant concentration (log c) for different surfactants.

$$\frac{dW_A}{d\gamma_{LG}} = \frac{d\gamma_{SG}}{d\gamma_{LG}} - \frac{d\gamma_{SL}}{d\gamma_{LG}} + 1 \qquad (4.12)$$

From the Gibbs adsorption equation, $d\gamma_{SG}/d\gamma_{LG} = \Gamma_{SG}/\Gamma_{LG}$ and $d\gamma_{SL}/d\gamma_{LG} = \Gamma_{SL}/\Gamma_{LG}$. Assuming, $\Gamma_{SG} \approx 0$, when there is equal surface excess on both the interfaces $\Gamma_{SL}/\Gamma_{LG} = 1$, $dW_A/d\gamma_{LG} \neq 0$ or W_A = constant. So, it can be assumed that the work of adhesion will not change with the concentration of surfactant. Since it is shown before, for this study, $\Gamma_{SL}/\Gamma_{LG} < 1$

or $dW_A / d\gamma_{LG} \neq 0$, indicates the work of adhesion will change with the concentration of surfactants.

To further analyze the results for the work of adhesion, it was observed that, although the contact angle decreases in the presence of surfactant solutions, the work of adhesion also decreases simultaneously. In general, from a basic understanding, with the decrease in contact angle, the wetting property enhances; as a result, the work of adhesion increases. This result can be attributed to the fact that, initially, the contact angle on the PTFE surface in the presence of water and low surfactant concentration is above 90º, where cos θ values are negative. As a result, the (1 + cos θ) term increases gradually with the decrease in contact angle. At the same time, the surface tension also decreases gradually. The decrease in surface tension is greater than the increase in the (1 + cos θ) term; as a result, the work of adhesion values decrease with increasing concentration.

4.3.8 Hamaker Constant for PTFE-Water Interaction

The experimental determination of the Hamaker constant (A) for a given material in surfactant solution can be useful for discussing the interaction between solid and liquid. When the Hamaker constant is positive (A > 0), it corresponds to an attraction between the molecules, and when it is negative (A < 0), it corresponds to repulsion. The constant of the PTFE-water system can be written as (Johnson and Dettre, 1993)

$$A_{PTFE-water} = 12\pi d^2 \gamma_{LG}(1+\cos\theta) \qquad (4.13)$$

Where d is the distance between the atoms contact. Literature values of Hamaker constant in vacuum for water and PTFE are A_{water} = 3.8 × 10 $^{-20}$ J and A_{PTFE} = 4.4 × 10 $^{-20}$ J respectively. Applying the Bertholet relation (geometric mean approximation) Hamaker constant for PTFE-water system can be calculated as, $A_{PTFE\text{-}water} = \sqrt{A_{water} \times A_{PTFE}} = \sqrt{3.8 \times 4.4} \times 10^{-20}$ J = 4.08 × 10 $^{-20}$ J. Using this $A_{PTFE\text{-}water}$ value, contact angle, and surface tension for pure water in equation (4.13) one can get d = 0.17 nm. Further, $A_{PTFE\text{-}water}$ was calculated in the presence of surfactant solution and presented in Figure 4.10. Similarly to the plot for the work of adhesion, there are slight irregularities at low surfactant concentrations, but at higher concentrations, there is a sharp decrease in Hamaker constant with increasing concentration, ultimately reaching a

plateau region close to the CMC of the individual surfactants. Throughout the concentration range studied, Igepal CO-630 exhibited lower values than TX-100.

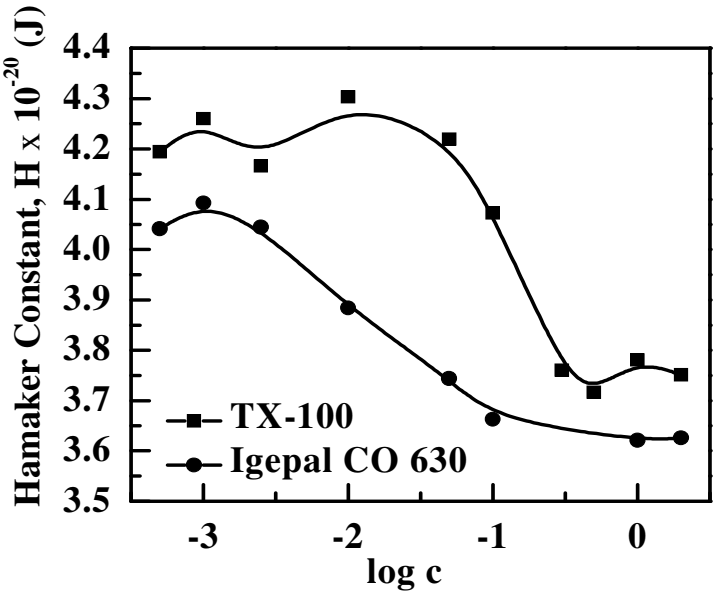


Figure 4.10 Change in the Hamaker constant (H) with concentration (log c) for different surfactants.

4.3.9 Wetting Free Energy of PTFE Surface

As the energy of the PTFE surface is low, wetting is difficult using only water, which has a high surface energy (~71.50 mN/m). In the presence of surfactant solution, the surfactant molecules adsorb on the PTFE surface and make it hydrophilic by increasing the surface energy. In this process, knowledge of the change in wetting free energy is also very important; larger values of the negative wetting free energy are expected to enhance the wetting process. From the thermodynamic point of view, the molar wetting free energy of the solid can be calculated according to Extrand (2003) as

$$\Delta G = \frac{RT}{3} ln \frac{(1-cos\,\theta)^2 (2+cos\,\theta)}{4} \qquad (4.14)$$

Figure 4.11 shows that, with the increase in surfactant concentration, the wetting free energy becomes more negative and ultimately reaches a constant value above the CMC.

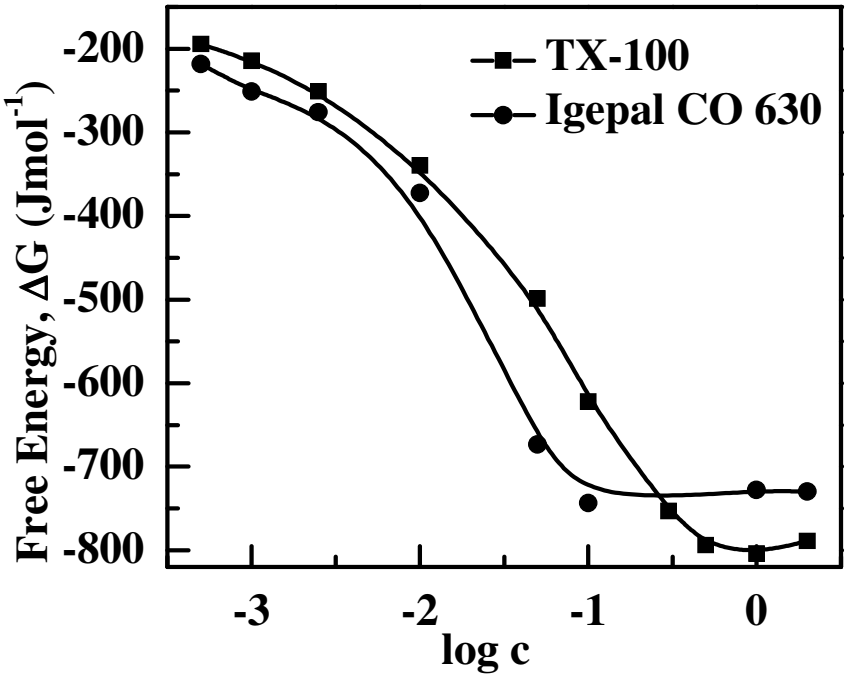


Figure 4.11 Change in the surface wetting free energy (ΔG) with concentration (log c) for different surfactants.

4.3.10 Polar and Dispersion Forces of Surfactant Solutions

According to Fowkes, (1963) the interfacial tension is the contribution of polar and dispersion forces. The air–water interfacial tension or surface tension can be written as

$$\gamma_{LG} = \gamma_L^P + \gamma_L^d \tag{4.15}$$

Where γ_L^d is the contribution of dispersive forces and γ_L^p is the contribution of polar interaction term (mostly contribution of hydrogen bonding). Specifically, at the PTFE-water interface interfacial tension can be defined by the geometric mean of the dispersive force components as

$$\gamma_{SL} = \gamma_{SG} + \gamma_{LG} - 2\sqrt{\gamma_L^d \gamma_S^d} \tag{4.16}$$

Where γ_S^d is the contribution of dispersive forces of PTFE.

Rearranging the equation,

$$W_A = 2\sqrt{\gamma_L^d \gamma_S^d} \tag{4.17}$$

At PTFE-air interface a similar equation to that of equation 4.15 can be written by neglecting the polar component of surface tension, $\gamma_{SG} = \gamma_S^d = 20.24$ mN/m (Szymczyk and Janczuk, 2007).

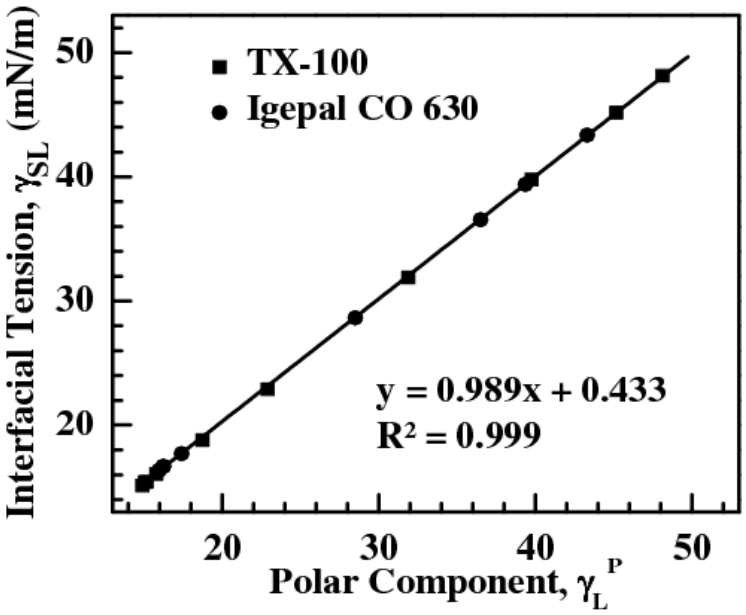


Figure 4.12 Plot of PTFE-water interfacial tension as a function of the polar component of the surface tension for different surfactants.

Since the work of adhesion and γ_{LG} values are known for each surfactant concentration γ_L^d value can be obtained from equation 4.15 and substituting the value in equation 4.15 γ_L^p can be calculated. The plot of γ_L^p vs. γ_{SL} for both the surfactants shows (Figure 4.12) there is a linear relationship exists, $\gamma_{SL} = 0.989\gamma_L^p + 0.433$. Since the direct determination of solid-liquid interfacial is difficult experimentally, however there is good linear relationship between the polar component of liquid and solid-liquid interface; γ_{SL} can be calculated by knowing the polar component of the solution. It has also been observed that the relationship is independent of the types of surfactants; certain value of γ_{SL} can be obtained by maintaining a particular polar component of the liquid.

4.4 Conclusions

The adsorption kinetics and isotherms of TX-100 and Igepal CO-630 were found to follow pseudo-second-order kinetics and the Langmuir isotherm model, with a higher adsorption constant rate constant and a higher Langmuir constant for Igepal CO-630. The decrease in contact angle with increasing surfactant concentration follows a trend similar to that of the adsorption isotherm of the respective surfactant. The free energy of wetting becomes more negative with increasing surfactant concentration, indicating that the process is spontaneous for

both surfactants. The Hamaker constant and work of adhesion decrease gradually with increasing surfactant concentration and ultimately reach plateau regions above the CMC. Igepal CO-630 shows a lower work of adhesion and Hamaker constant than TX-100. The change in the polar component of the interaction term with the PTFE-water interfacial tension follows the same linear relationship for both surfactants, so the PTFE-water interfacial tension is independent of the type of surfactant. Igepal CO-630 has a lower CMC value and better wetting properties at low concentration than TX-100, as well as comparable properties near the CMC. As a result, the use of Igepal CO- 630 as a wetting agent might be more beneficial than the use of TX-100 because of lower consumption in the process and possibly higher biodegradability in nature (because of the presence of a straight-chain hydrocarbon tail).

Chapter 5

Wetting of PTFE and Glass Surfaces by Aqueous Solutions of Cationic and Anionic Double-Chain Surfactants

Chapter 5

Wetting of PTFE and Glass Surfaces by Aqueous Solutions of Cationic and Anionic Double-Chain Surfactants

5.1 Introduction

Wetting of solid surfaces by surfactant solutions is important for many applications. The reported studies show there have been extensive studies on wetting of low-energy (hydrophobic) solid surfaces (Szymczyk and Janczuk, 2006; Biswal and Paria, 2011), compared to high-energy (hydrophilic) solid surfaces (Zdziennicka et al., 2009; Zhang et al., 2010), using different surfactants. Surfactant solutions play an important role in the wetting process by changing water surface tension and solid−water interfacial tension because of adsorption of surfactant molecules at the interfaces. Most of the wettability studies on solid surfaces are focused on aqueous solutions of different single-chain surfactants (Zhang et al., 2010; Biswal and Paria, 2011), the effect of different additives (Zdziennicka et al., 2005; Chaudhuri and Paria, 2009), and mixed surfactants (Szymczyk and Janczuk, 2007; 2008) but are rare on double-chain surfactants (Cao et al., 2006; Lai and Chen, 2008). Double-chain surfactants are generally of two hydrocarbon chains on a headgroup or dimeric with two head groups (Gemini). Double-chained surfactants have continued to have more and more scientific interest over the past one or two decades because of their superiority over the single-chain surfactants. The reported studies show Gemini surfactants have many superior features such as good water solubility, low critical micelle concentration (CMC), low Krafft point (at this temperature the solubility of the surfactant is equal to the CMC, below which the surfactant remains in crystalline form), and excellent surface activity in aqueous solution compared to conventional single-chain surfactants due to their unique structures (Zana, 2002). Additionally, the nature of the spacer group is also most important in determining the solution properties of Gemini surfactants. Reported data on solution behavior of different Gemini surfactants show although they have low CMC values of 0.00591−0.093 mM (Tsubone, 2003; Kolaya et al., 2009; Kabir-ud-Din et al., 2006; Acharya et al., 2005; Zhao et al., 2006), only a few have a low minimum surface tension value (≤25 mN/m) at CMC compared to conventional single-chain surfactants (Tsubone, 2003; Acharya et al., 2005). Similarly double-chain surfactants also show superior surface activity compared to

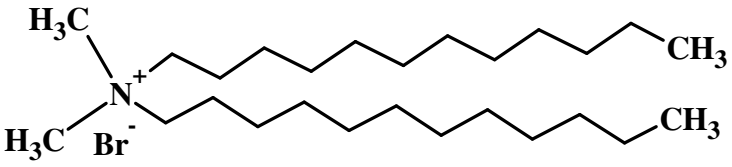
conventional single-chain surfactants because of similar reasons mentioned before. However, most of the double-chain surfactants show a comparatively lower minimum surface tension value than the Gemini surfactants (Marques et al., 1999; Grillo et al., 2009). There are several studies available on the wettability of single-chain surfactants on hydrophilic and hydrophobic surfaces but a limited number on Gemini (Cao et al., 2006; Seredyuk et al., 2002; Pisarcik et al., 2005; Ao et al., 2009) or double chain surfactants (Lai and Chen, 2008; Harkot and Janczuk 2008; Pyter et al. 1982; Bascha and Strnad, 2011; Bi et al., 2005). Seredyuk et al. (2002) have studied the wettability of a zwitterionic Gemini surfactant of dissimilar chain lengths on a porous paper surface. Cao et al. (2006) studied the wettability of cationic Gemini surfactant $[C_{12}–C_6–C_{12}]Br_2$ on silica surface and showed initially there was an increase in contact angle (51–63°) with the increase in surfactant concentration, which then again decreased to 31° because of formation of surface aggregation by the surfactant molecules. A similar observation was also found using imidazolium Gemini surfactant ($[C_{12}–C_4–C_{12}im]Br_2$) on the silicon wafer surface with a minimum contact angle of ∼41°.21 They also reported the contact angle decreases until the concentration of 5 CMC because of the formation of multilayer adsorption. The wettability of anionic double-chain surfactant aerosol OT (AOT) was studied on both the low surface energy hydrophobic (PTFE and PMMA) and hydrophilic (glass) surfaces (Szymczyk and Janczuk, 2006; Pisarcik et al., 2005; Harkot and Janczuk 2008). Harkot and Janczuk (2008) found the surfactant formed a monolayer adsorption on the solid–water interface and adsorption density at air–water and PTFE–water interfaces were equal. However, the adsorption densities at PMMA–water and glass–water interfaces were different from that of the air–water interface. Wettability on powder surfaces (alumina, silica) was also reported using double-chain surfactants (Bascha and Strnad, 2011; Bi et al., 2005). Bi et al. (2005) synthesized a double-chain surfactant, N,N-dipalmitoylethylenediaminediacetic acid sodium salt ($Di_{16}EDDA$), and it was found to have very good wetting property on silica powder compared to AOT. In this chapter we report on the wetting of PTFE and glass surfaces using aqueous solutions of cationic (DDAB) and anionic (AOT) double-chain surfactants. The novelty of this work is that wettability of anionic and cationic two double chain surfactants on hydrophobic and hydrophilic surfactants is studied, and the values are compared with the reported studies of different single-chain surfactants. The study shows the use of cationic double-chain surfactant would be more effective for wetting of the

PTFE surface than the conventional single-chain surfactants, which in turn may indirectly reduce the environmental problem as well as the process cost.

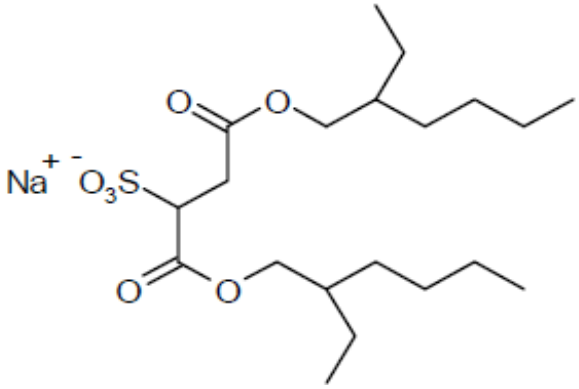
5.2 Materials and Methods

5.2.1. Materials

The cationic double-chain surfactants, di-dodecyldimethyl ammonium bromide (DDAB) and anionic double-chain surfactants, Aerosol OT (AOT) were purchased from Sigma–Aldrich chemicals, Germany (Cat no. 93418 and 542334 respectively) and used without any further purification. The structures of the surfactants are presented in Figure 5.1.



(a)



(b)

Figure 5.1 Structure of double-chain surfactants: (a) DDAB and (b) AOT.

5.2.2. Methods

5.2.2.1. Measurement of Surface Tension and CMC

The surface tension and CMC of the surfactants were measured according to the method described in section 3.2.2.1.

5.2.2.2. Measurement of Contact Angle

The contact angle of the surfactants on PTFE and Glass surfaces were measured according to the method described in section 4.2.2.3.

5.2.2.3. FT-IR Spectroscopy

Transmission infrared spectra were obtained using a FT-IR spectrophotometer (IRPrestige-21, Shimadzu, Japan) in transmission mode, after the PTFE and Glass slides were left to equilibrate

in 1 mM DDAB surfactant solutions for 3 hr and dried at 50º C. The spectra were taken at 4 cm^{-1} resolution. Background spectra were obtained using bare PTFE and Glass slides.

5.3 Results and Discussion

5.3.1 Surfactant Adsorption at Air-Water Interface

The adsorption efficiency of surfactant molecules at the air–water interface is generally considered as an indicator of surface activity of a surfactant. The surface tension values of the double-chain cationic and anionic surfactant solutions versus logarithm of concentrations are presented in Figure 5.2.

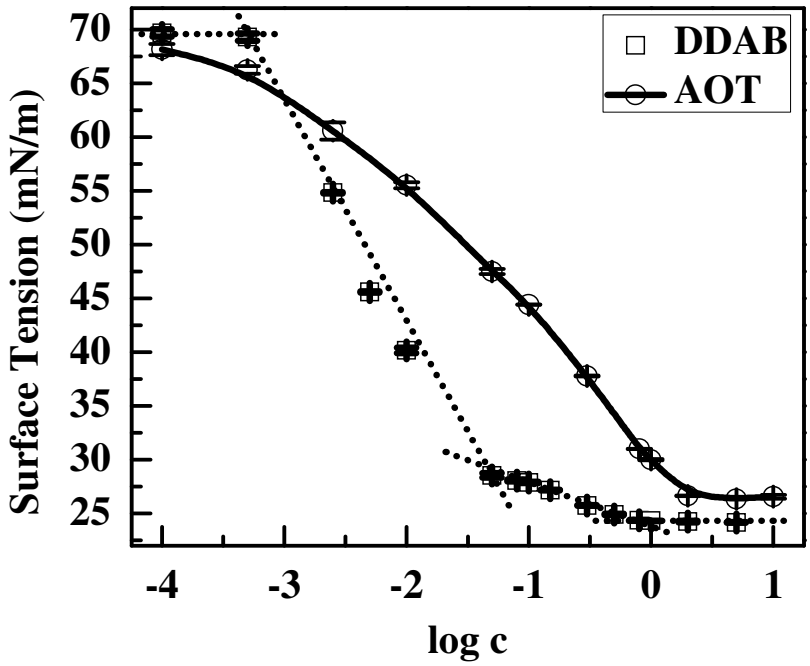


Figure 5.2 Change in surface tension (mN/m) with the concentration (log c) of different surfactants.

The figure depicts the solution behavior with the increasing concentrations are different for two double-chain surfactants studied here. AOT shows there is a gradual decrease in surface tension until the CMC; beyond that concentration surface tension values are almost constant, similar to the conventional single-chain surfactants. In contrast, DDAB shows two transition points. Initially there is a sharp decrease in surface tension and then a change of slope at 0.05 mM (log c = −1.3); further at 0.8 mM (log c = −0.09) a second break of slope is observed. The first break is because of the formation of the micelle in the solution, and the second break point of the surface tension corresponds to the transition from micelles to small unilamellar or large multilamellar

vesicles, referred to as a critical vesicle concentration (CVC) (Grillo et al., 2009). The slopes of the linear portion of log c vs surface tension plot of two different regions are −20.77 and −3.91 for DDAB, indicating the slope in the micellization region is much greater than the region for vesicle formation. While comparing the slopes of the first region for two surfactants, it is observed that DDAB has a much higher slope than AOT (−9.83). The minimum surface tension value obtained for DDAB was also lower (24.36 mN/m) than AOT (26.351 mN/m); at the same time DDAB was also having much lower CMC (0.05 mM) than AOT (2 mM). On the other hand, these surface tension values are also significantly lower than the conventional single-chain cationic (CTAB = 32.99 mN/m), anionic (SDBS = 34.22 mN/m) (Ghosh Chaudhuri and Paria, 2009), and nonionic (TX-100 = 31.01 mN/m, Igepal CO-630 = 31.02 mN/m) (Biswal and Paria, 2011) surfactants frequently used for several applications. Since lowering of surface tension to a lesser extent is an important criterion to show the better surface activity of any surfactant, these surfactants are expected to have better interfacial properties. The area occupied per molecule for DDAB and AOT was calculated using Gibbs adsorption equation from the surface tension data below the first break point region. The values obtained are 91 and 192 $Å^2$/molecule for DDAB and AOT, respectively. Lower area per molecule also indicates the closer packing of DDAB molecules at the air−water interface.

5.3.2 Wetting of DDAB and AOT on PTFE and Glass Surfaces

The changes in advancing contact angle values with the increasing concentration (log c) of DDAB and AOT are presented in parts a and b of Figure 5.3, respectively, for PTFE and glass surfaces. Figure 5.3a clearly shows the dependency of contact angle with the logarithm of concentrations on the PTFE surface, which is similar to that of the surface tension for both surfactants.

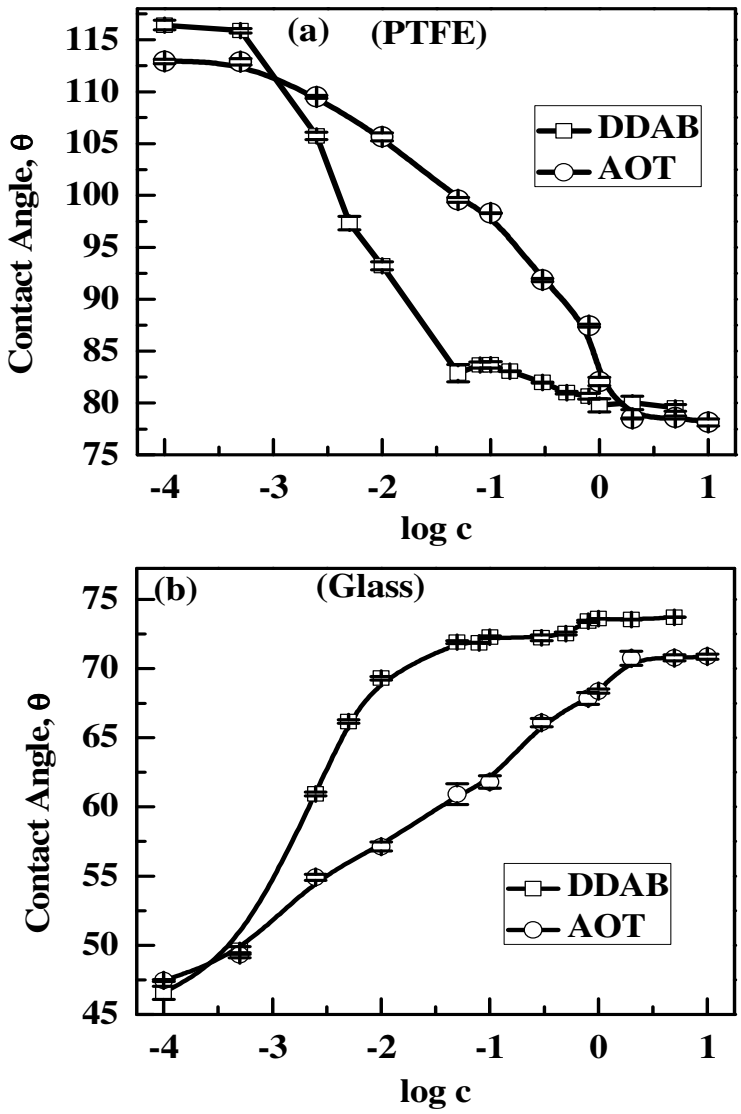


Figure 5.3 Change in contact angle (θ) with the concentration (log c) of different surfactants on (a) PTFE and (b) glass surfaces.

For the DDAB surfactant first and second slopes are −16.85 and −3.30, respectively, whereas for AOT it is −9.00. The minimum contact angle values obtained were 79 and 78.5° for DDAB and AOT, respectively, compared to 116.5° for pure water. So the total decrease in contact angle is ~38° with respect to pure water for both surfactants. The contact angle in the presence of DDAB is 83° at CMC, and above that concentration at CVC the value reduces to 79°. The limiting contact angle values are very close for both surfactants, but the final concentration is 2.5 times lower for DDAB (0.8 mM) than AOT (2 mM). It can also be observed that the final contact angle values for both double-chain surfactants are significantly lower than the commonly used

cationic (CTAB = 84.06°), anionic (SDBS = 86.76°) (Ghosh Chaudhuri and Paria, 2009), and nonionic (TX-100 = 81.08°, Igepal CO-630 = 83.33°) surfactants (Biswal and Paria, 2011). The gradual decrease in the contact angle values are similar to that of the change in surface tensions, indicating probably DDAB and AOT molecules are adsorbed as a monolayer on the PTFE surface; the formation monolayer adsorption of DDAB on PTFE surface was also reported before (Yao and Strauss, 1992). If the consumption surfactants are calculated for wetting with reference to the concentration where plateau level contact is achieved, it can be found that the DDAB consumption is 60% lower than AOT and similar to CTAB but the minimum contact angle is 5° lower than CTAB. However, if the comparison is made at a particular contact angle of 84° (minimum achieved by CTAB), then the consumption of DDAB is 93% lower. In the case of the hydrophilic glass surface AOT shows there is a linear increase in contact angle with the increase in the logarithm of the surfactant concentration, and when the concentration is above 2 mM, the contact angle reaches to a plateau level (Figure 5.3b). The change in contact angle is 46.5° (pure water) to 70.7°. In the presence DDAB initially there is a rapid increase in contact angle until the concentration of 0.01 mM, above that concentration the rate of increase is slower; finally above 0.8 mM concentration the contact angle reaches a steady value of 73°. Both surfactants show slightly higher contact angle values than the conventional different single-chain surfactants such as cationic (CTAB = 62.5°), anionic (SDBS = 59.33°), and nonionic (TX-100 = 68.8°, Igepal CO630 = 68.68°). From Figure 5.3b it can be observed that the adsorption of surfactant makes the hydrophobic PTFE surface to hydrophilic and exactly reverse for the hydrophilic glass surface. Previously reported contact angle studies using single-chain cationic surfactants on a glass surface showed initially there was an increase in contact angle and then again a decrease with the increase in surfactant concentration because of the formation of an adsorbed bilayer on the surface (Zhang et al., 2010). However, the present study shows no decreasing trend in the contact angle at higher surfactant concentration, indicating the probable monolayer adsorption of DDAB on the glass surface; as a result there is a gradual increase in hydrophobicity. The monolayer formation of DDAB is also consistent with the findings of Lu et al. (2008) for adsorption of DDAB at the silica surface. They have reported the formation of surfactant monolayer on the silica surface, and the molecular parking area was ~0.9 times of monolayer in the saturation level obtained from the air−liquid interface. In the present study the lower saturation level (0.84 times, discussed in section 5.3 on the glass surface can be attributed

to a lower surface area of the flat surface compared to small particles reported before (Lu et al. (2008)), less contact time (~25 s) between the solid surface and surfactant solution during the dynamic contact angle measurement. The schematic diagram of the adsorption layers on glass and PTFE surfaces using double-chain surfactants is shown in Figure 5.4.

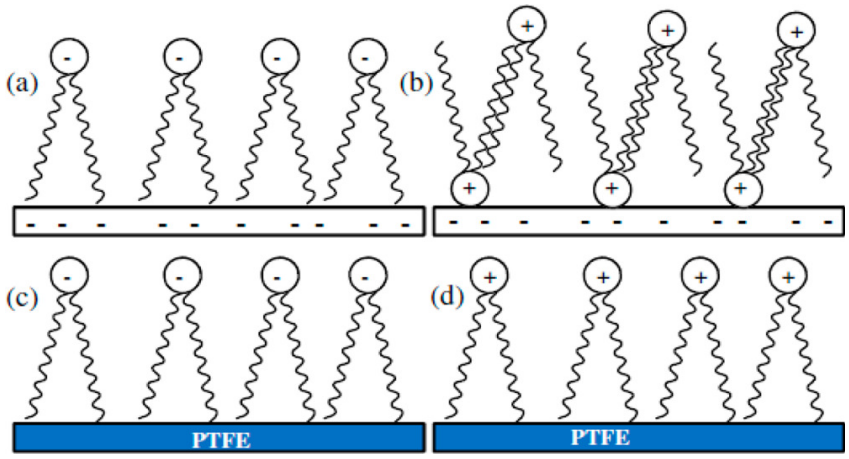


Figure 5.4 Schematic diagram of the adsorption layer of double chain surfactants: (a) AOT on the glass, (b) DDAB on the glass, (c) AOT on the PTFE, and (d) DDAB on the PTFE surfaces.

5.3.3 Characterization of Surfactant Adsorption on PTFE and Glass Surfaces by FTIR

To get some qualitative idea about the arrangement of the adsorbed surfactant molecules on PTFE and glass surfaces in terms of molecular interaction, FT-IR analysis was done for DDAB. Because the methylene ($-CH_2$) vibration is sensitive to the molecular interaction of the hydrophobic chains, the peak position of the methylene stretching can be used to get an idea about the adsorption pattern of the surfactant molecules on the solid surface.

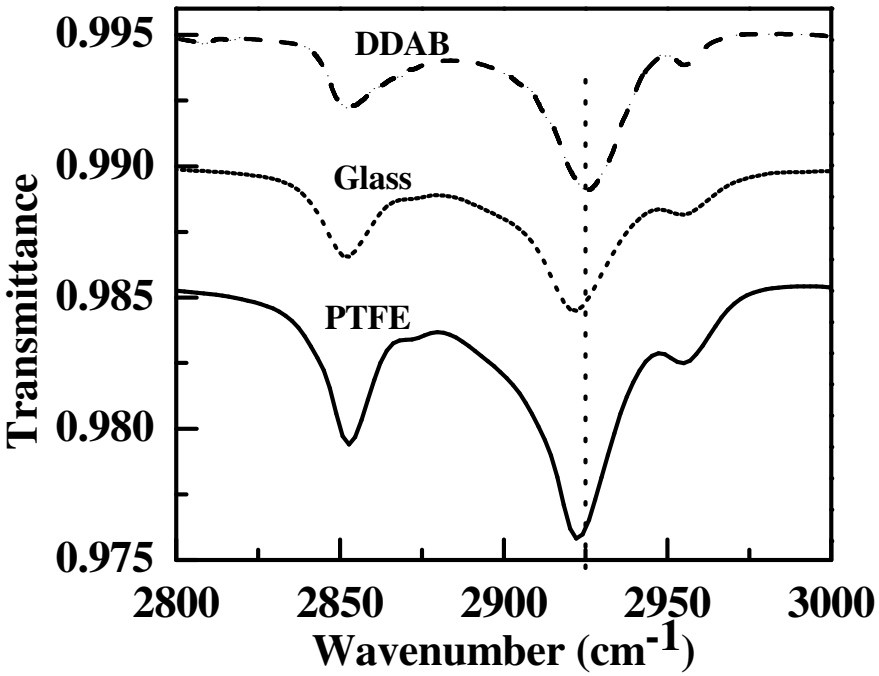


Figure 5.5 FT-IR spectra of DDAB on PTFE and glass surfaces.

Figure 5.5 shows the FT-IR spectra of surfactant molecules on the PTFE surface after dipping in 1 mM DDAB solution for 3 h equilibrium time. For pure DDAB surfactant the -CH_2 asymmetric (ν_{as}) and symmetric (ν_s) vibration bands were obtained at ~2926 and ~2855 cm^{-1}, respectively. These values are close to those of reported values of 2926 and 2853 cm^{-1} respectively for octadecyltrimethylammonium bromide (C_{18}TAB) surfactant (Mellott et al., 2004; Hayes and Schwartz, 1998). After adsorption of surfactant on PTFE surfaces it was found that the ν_{as} and νs vibration bands shifted toward lower wavenumber, obtained at ~2922 and ~2852 cm^{-1}, respectively. A 4 cm^{-1} shift in ν_{as} vibration band toward lower wavenumber may be attributed to tail−tail interaction between the surfactant molecules because of the close-packed adsorption of molecules on the PTFE surface, which in turn reduced the freedom of the surfactant molecules as well as stretching vibrations. After adsorption of surfactant on the glass surface it was found that the ν_{as} and ν_s vibration bands of the methylene (-CH_2) group were obtained at ~2922 and ~2852 cm^{-1}, similar to that of the PTFE surface. On the glass surface, although the adsorption pattern is reverse, the shift in vibration bands may be because of a similar tail−tail interaction of surfactant molecules as suggested schematically in Figure 5.4.

5.3.4 PTFE–Water and Glass-water Interfacial Tension

Adsorption of surfactant at air–water and solid–water interfaces changes the surface or interfacial tensions at the respective interfaces, which is again closely related to wetting of a solid surface. The contact angle can be related to the surface or interfacial tensions using Young's equation as mentioned in equation (4.7) of chapter 4.

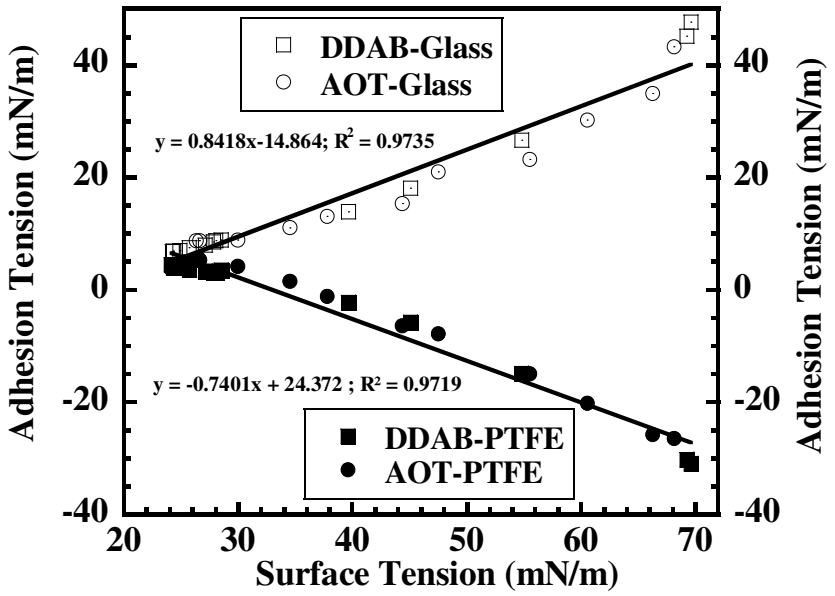


Figure 5.6 Plot of surface tension (mN/m) vs adhesion tension (mN/m) of DDAB and AOT on PTFE and glass surfaces.

To get a relationship between the contact angle and surface excess at the interfaces Young's and Gibbs equations can be combined as mentioned in equation (4.8) of chapter 4. If the surface excess at the solid-air interface is assumed to be zero ($\Gamma_{SG} = 0$, because there is no contact with the solution), the ratio of surface excess at the solid-water and air–water interfaces (Γ_{SL}/Γ_{LG}) can be obtained from the slope of $\gamma_{LG} \cos \theta$ or adhesion tension versus γ_{LG} plot. The surface excess values of surfactants at the solid-water and air–water interfaces are dependent on the slope of the linear relationship; such as $\Gamma_{SL} = \Gamma_{LG}$ (slope = 1), $\Gamma_{SL} > \Gamma_{LG}$ (slope > 1), and $\Gamma_{SL} < \Gamma_{LG}$ (slope < 1). The plots of adhesion tension versus surface tension for DDAB and AOT show there are linear relationships on both the PTFE and glass surfaces (Figure 5.6). The average slopes on PTFE and glass surfaces are −0.759 (DDAB = −0.745, AOT = −0.775) and +0.840 (DDAB = 0.831, AOT = 0.854), respectively. These results qualitatively demonstrate that the surface excesses at both the solid−water interfaces are less than that at the air−water interface for both the double-chain surfactants. The unequal surface excesses at PTFE−water and air−water

interfaces were also reported before for the single chain surfactants (Biswal and Paria, 2011; Ghosh Chaudhuri and Paria, 2009).However, while comparing the slopes obtained from the present to our previous studies, it can be concluded that these double-chain surfactants are having less surface excess at the solid−water interface than the air−water interface. The reported values of the $\Gamma_{PTFE-water}/\Gamma_{air-water}$ ratio using different single-chain surfactants, such as Igepal CO-630, TX-100, CTAB, and SDBS are in the range of 0.83−0.86 (Biswal and Paria, 2011; Ghosh Chaudhuri and Paria, 2009). This fact can be attributed to the adsorption pattern of surfactant molecules on the PTFE surface. At the air−water interface double-chain surfactant molecules are giving a better close packing structure, keeping the tailgroup outward direction because of greater hydrophobic interaction between the tailgroups of the surfactant molecules. However, at the PTFE−water interface double-chain surfactant, molecules adsorbed with less flexibility compared to single-chain molecules, which mostly make a monolayer, as a result, lowers molecular density. The results of the glass−water interface show the linear relationship between the adhesion tensions versus surface tension with an average slope of 0.84, indicating unequal adsorption at glass−water and air−water interfaces. The studies on single-chain surfactants showed the slope was different for each individual surfactant; the cationic surfactant also showed higher adsorption density at the solid−water interface ($\Gamma_{SL}/\Gamma_{LG} > 1$), attributed to the formation of multilayer adsorption (Ghosh Chaudhuri and Paria, 2012). In contrast, for both the cationic and anionic double-chain surfactants, the surface excess at the glass−water interface is a little higher than the PTFE−water interface, but still less than that of air−water interface, maybe because of the monolayer adsorption as discussed before. Figure 5.6 clearly shows there is a crossover point between the adhesion tensions on PTFE and glass surfaces. The crossover point is at 25 mN/m surface tension and 5 mN/m adhesion tensions. Since the minimum surface tension of 25 mN/m is achieved by DDAB at CMC, so the crossover point occurs in the presence DDAB where both the surfaces are having the same adhesion tension. In contrast, our previous studies using nonionic surfactants (Igepal CO-630 and TX-100) showed there was no crossover point, as those surfactants could not reach to that much lower surface and adhesion tensions. This may be called as critical adhesion tension for the solid−water interfaces, where both the hydrophilic and hydrophobic surfaces are having equal adhesion tension and wetting toward a particular surfactant solution. The area occupied per surfactant molecules at any interface can give some idea about the packing as well as the orientation pattern. The area occupied per

molecule (A_{air}) of DDAB and AOT is found to be 91 and 192 Å^2, respectively, mentioned before. Since the surface excess of the surfactant at the PTFE– water interface is 0.75 times less than that of the air–water interface, hence, the areas per surfactant molecules at the PTFE–water interface are 121.33 and 256 Å^2 for DDAB and AOT, respectively. Similarly, because the surface excess of surfactants at the glass–water interface is 0.84 times lower than that of air–water interface, the values of A_{glass} obtained are 108 and 229 Å^2 for DDAB and AOT, respectively. The molecular density results indicate double-chain surfactant solutions are able to change the contact angle on hydrophilic and hydrophobic surfaces to a greater extent than the single-chain surfactants although the area occupied per molecule is less for the former case.

5.3.5 Work of Adhesion of Surfactants Solutions

The work of adhesion of a liquid to solid, W_A, is defined by the reversible work required to separate a unit area of liquid from a solid surface and can be calculated by using the equation (4.10) and (4.11)

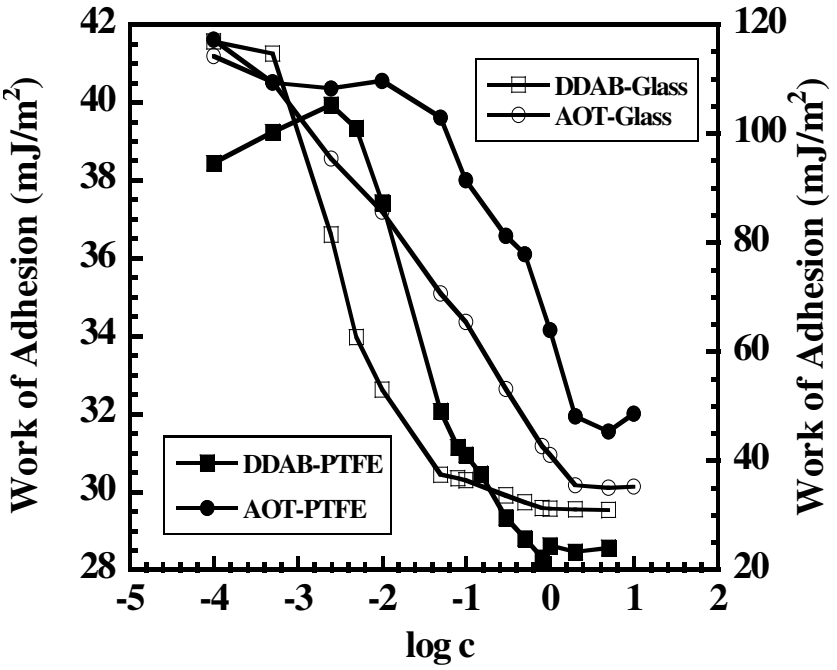


Figure 5.7 Change in work of adhesion (W_A) with the concentration (log c) of different surfactants.

The work of adhesion of surfactant solutions on PTFE and glass surfaces was calculated by putting the contact angle and surface tension values in equation (4.11) and presented in Figure 5.7. From the figure it can be observed that the work of adhesion (W_A) decreases with the

increasing concentration of surfactants (DDAB and AOT) on both PTFE and glass surfaces. While comparing the adhesion tensions of DDAB and AOT on the PTFE surface, it can be found that adhesion tension in the presence of DDAB is lower than AOT. In contrast, on the glass surface, DDAB shows lower adhesion tension below the CMC region, but the difference is not very significant above the CMC region. The work of adhesion of pure water for PTFE and glass surfaces is 39.59 and 120.71 mJ/m^2, respectively. The work of adhesion of DDAB solutions on PTFE and glass surfaces above the CMC is 28.55 and 30.94 mJ/m^2, respectively, whereas that of AOT solutions on PTFE and glass surfaces is 32 and 35.24 mJ/m^2, respectively, above the CMC.

5.3.6 Wetting Free Energy on PTFE and Glass Surfaces

The surface free energy quantifies the strength of interaction of the spread liquid onto the solid surface. From the thermodynamic point of view the molar wetting free energy of the solid can be calculated using equation (4.14).

The free energies of wetting on the PTFE surface are more negative ($\Delta G_{PTFE-DDAB}$ = −831.73 J/mol; ($\Delta G_{PTFE-AOT}$ = −871.66 J/mol) in the presence of surfactant solutions above the CMC than pure water (−171.54 J/mol). However, on the glass surface the free energies of wetting are less negative ($\Delta G_{glass-DDAB}$ = −1007.63 J/mol; $\Delta G_{PTFE-AOT}$ = −1102.97 J/mol) than pure water (−2253.88 J/mol). But the surface free energies of glass for both the surfactants are more negative compared to the PTFE surface.

5.4 Conclusions

Double-chain cationic (DDAB) and anionic (AOT) surfactants show a lower value of minimum surface tension at the CMC compared to that of commonly used single-chain surfactants. The plot of surface tension vs concentration of DDAB shows two break points in slope because of the formation of micelle first and then vesicle, with higher slope at the micellar region. The surfactant concentration to achieve plateau level surface tension and the minimum surface tension values are lower for DDAB than AOT; subsequently adsorption density of DDAB is higher at the air−water interface than AOT. The wettings of the PTFE surface in the presence of both the double-chain surfactants are similar in terms of a decrease in contact angle and much better than the conventional single-chain surfactants; however, the final concentration required for DDAB is lower than AOT. In the case of the glass surface the increase in contact angle is

slightly more for DDAB. There is a linear relationship of adhesion tension and surface tension with slopes of −0.759 and +0.840 on PTFE and glass surfaces, respectively, for both surfactants; the slope values below one indicate surface excess of surfactant molecules at the solid−water interfaces are less than that of the air−water interface. DDAB solutions show a critical adhesion tension for the PTFE−water and glass− water interfaces, where both the hydrophilic and hydrophobic surfaces are having equal adhesion tension and wettability. The free energies of wetting on the PTFE surface are more negative in the presence of surfactant solutions than pure water. However, on the glass surface the free energies of wetting are less than pure water but free energies of wetting on the glass surface are still more negative than PTFE for both surfactants. Finally, it can be concluded that the double-chain cationic and anionic surfactants are having better wettability on the PTFE surface compared to single-chain surfactants. The use of cationic double-chain surfactant (DDAB) may reduce the consumption of surfactant to a value of 93 and 60%, respectively, compared to that of CTAB and AOT for wetting of the PTFE surface.

Chapter 6

Adsorption and Wetting Behavior of Natural surfactants on PTFE surface

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Chapter 6

Adsorption and Wetting Behavior of Natural surfactants on PTFE surface

6.1 Introduction

Wetting of low surface energy solid surfaces by polar liquids is a challenging task to the researchers because of its gradual increasing practical importance (Adamson, 1991; Adamson and Gast, 1997; Penner et al., 1999; Gecol et al., 2001; Kijlstra et al., 2002; He et al., 2004). The reported studies on wetting of hydrophobic surfaces by aqueous surfactant solutions can be broadly classified into two types based on the surfactant category: (i) synthetic surfactants, (ii) bio- or natural surfactants. The studies on synthetic surfactants are mostly concentrated on single-chain surfactants (Janczuk et al., 1997; Chaudhuri and Paria, 2009, Biswal and Paria, 2011), Gemini and double-chain surfactants (Pisarcik et al., 2005; Ao et al., 2009; Biswal and Paria, 2012; Harkot and Janczuk, 2007), surfactant and alcohol mixture (Zdziennicka et al., 2005; Zdziennicka and Janczuk, 2008a, b; Zdziennicka, 2008, 2009), surfactant and electrolytes mixture (Ghosh Chaudhuri and Paria, 2009), mixture of different surfactants (Zdziennicka et al., 2003; Szymczyk and Janczuk, 2006; Szymczyk et al., 2006; Szymczyk and Janczuk, 2007), and surfactant mixture in the presence of electrolytes (Ghosh Chaudhuri et al., 2012). The synthetic surfactants based studies mostly highlighted on fundamental aspects to explore the mechanism, to find the most effective surfactant for better wetting, enhancement of performance or reduction in consumption by the addition of additives or using mixed systems. In case of industrial or domestic application of these surfactants, when the consumption is more disposal of surfactant solutions after the application is a major environmental issue. Since the synthetic surfactants are not easily biodegradable or sometimes their biodegradable products are also more harmful, from the environmental viewpoint they are not well accepted. In the recent years an alternate thought and importance has been given on the application of environmentally friendly surfactants to reduce environmental problems.

In spite of the fact that there are large number of studies available on wettability of hydrophobic surfaces by synthetic surfactant solutions quite a few on that of environmentally friendly surfactants. There might be several reasons associated behind it such as limited number of surfactants are explored still today, performance may not be as good as that of the synthetic, limitation on bulk scale production, economically not viable and so on. Very few are there on

biosurfactant also (Ishigami et al., 1993; Ozdemira and Malayoglu, 2004). Ishigami et al. (1993) studied the wetting characteristics of rhamnolipids R–B–Na (sodium salt of rhamnolipid B) and its derivative R–B–Me (rhamnolipid B methyl ester) on five different kinds of polymer surfaces. They presented the measured contact angles as a function of increasing critical surface tension (γ_C) of polymer surfaces at two different R–B–Na and R–B–Me concentrations. Rhamnolipid B (RB) showed a small CMC, large surface tension reduction, notable interfacial tension lowering action for hydrocarbons, and wetting actions for biomembranes and polymers. When the carboxylic moiety of RB was converted to methyl ester (nonionic surfactant), the interfacial lowering and the wetting actions of RB were significantly enhanced. On the other hand, CMC and γ_{CMC} values increased. Ozdemir and Malayoglu (2004) have compared the wetting properties of anionic biosurfactants (rhamnolipids) with that of, sodium dodecyl sulfate (SDS) was chosen as the reference surfactant on a hydrophobic polymer, polyethylene terephthalate (PET) surface and found that at low concentration similar contact angle with SDS but above a certain concentration rhamnolipid shows better wetting at even an order of magnitude lower concentration. Parallel to this behavior, at low surfactant concentrations the adhesion tension decreased, then remained constant and an increase at higher surfactant concentrations was obtained on hydrophobic surfaces. They found that for the polymer surfaces with γ_c between 18.5 (PTFE) and 43 (PET) the contact angles remained almost constant at each R–B concentration, increasing only with the increase in R–B concentration. R–B molecules have three hydrophobic tails and they are more volumable molecules than R_1 and R_2.

This study focuses on the adsorption and wetting behavior of plant based three natural surfactants on PTFE surface. The effect of alcohol as additive on wetting behavior was studied. The major advantage of these plant based surfactants is large scale production is highly possible for practical applications compared to that of bio-surfactants from microorganism, as a result they might be economically more viable also. Since there is no study available still today on adsorption and wetting behavior of these plant surfactants on PTFE surface, to the best of knowledge, evaluation of their performance compared to the conventionally used surfactants and explore the mechanism would be highly useful for their practical applications to reduce environmental pollution.

6.2 Materials and Methods

6.2.1 Materials

Same as mentioned in section 3.2.1 and 4.2.1

6.2.2 Methods

6.2.2.1 Extraction of Plant Surfactants

The plant surfactants Reetha and Shikakai were extracted from the fruits according method mentioned earlier (Rao and Paria, 2009). Acacia was extracted first with methanol similar to those other two surfactants. The dry powder was then again extracted with mixture of methanol and ether to get a complete water soluble fraction.

6.2.2.2 Surface Tension Measurement

The surface tension and CMC of the surfactants were measured according to the method described in chapter 3.2.2.1.

6.2.2.3 Adsorption of Plant Surfactants on PTFE Surface

The surfactants adsorption kinetics and isotherm of on PTFE surface were measured according to the method described in chapter 3.2.2.2.

6.2.2.4 Dynamic Contact Angles Measurement

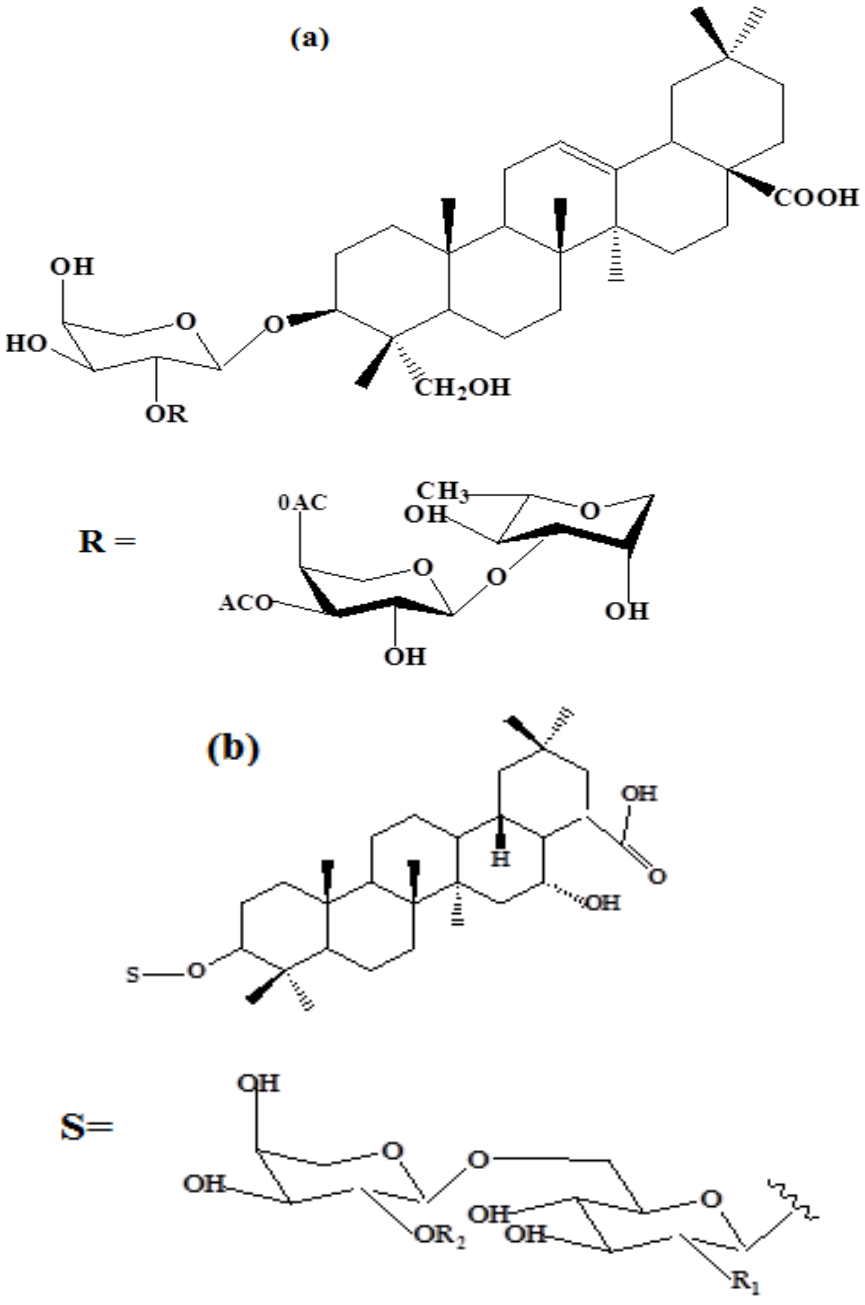
The contact angle of the surfactant solutions on PTFE surface were measured according to the method described in chapter 4.2.2.3.

6.3 Results and Discussion

6.3.1 Structure and Physical Properties of Plant Surfactants

Structures of the plant surfactants are most important to know before discussing the experimental results. Figure 1 (a) shows the structure of Reetha (*S. Mukorossi*) with a molecular weight of 966 as proposed in the reported study (Rao and Paria, 2009). The probable structures of Shikakai (*A. Concinna*) and Acacia (*A. Auriculiformis*) and shown in parts (b) (Gafur, et al., 1997; Tezuka ei al., 2000) and (c) (Mahato et al. 1992; Majhi et el. 1999) of Figure 1, they are also having molecular masses 1058 and 1765 respectively. The CMC value of both Reetha and Shikakai was found to be 0.5 mM at 25 °C measured by surface tension method. The CMC of Acacia was found 0.39 mM at 25 °C. The aqueous solutions of Reetha and Shikakai are little acidic, their pH values are 4.34 and 3.5 respectively; however, Acacia solution is neutral (pH = 6.5-7).

These surfactants are mostly nonionic in nature and the class of triterpenoid glycosides type (Balakrishnan, et al., 2006). The hydrophilic part mainly consists of sugars such as D-glucose, D-xylose, L-arabinose, L-rhamnose, and glucuronic acid (Row and Rukmini, 1966). Sapindic acid and oleanolic acid are the main constituents of the hydrophobic portion (Chatterjee and Pakrashi, 1997; Mitra and Dungan, 1997).



R_1= NHAc and R_2= α-L-Arabinose

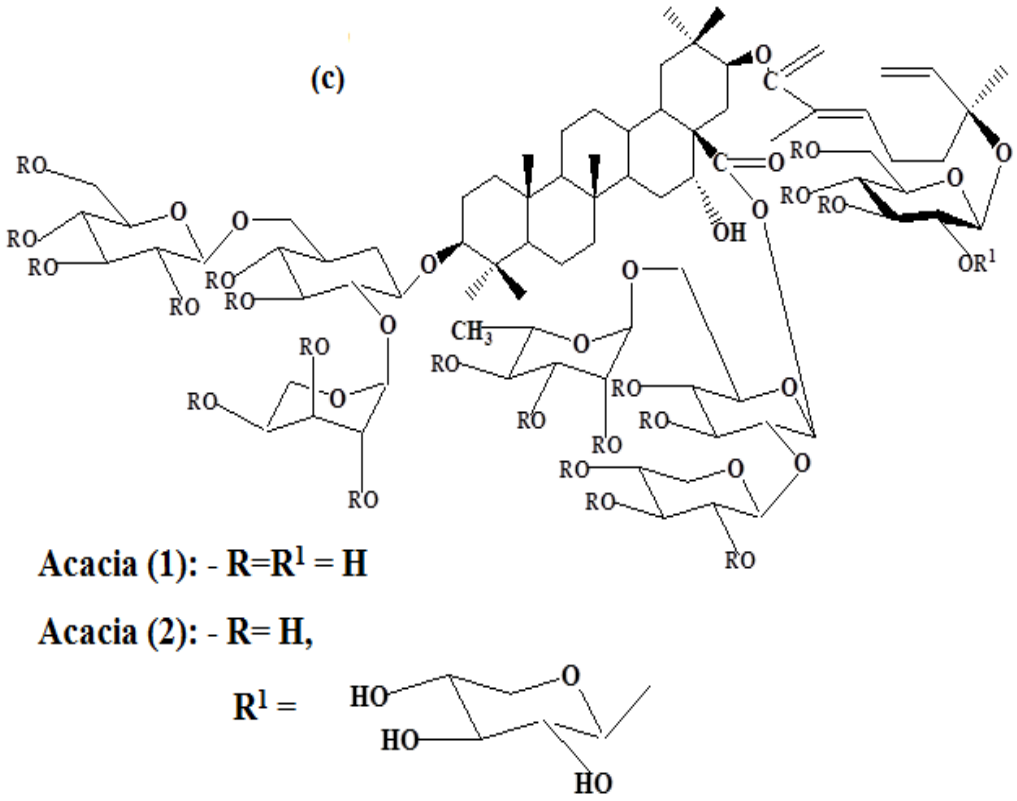


Figure 6.1 Structure of three plant surfactants, (a) Reetha, (b) Shikakai, (c) Acacia.

6.3.2 Adsorption of Plant Surfactants at Air-Water Interface

The surface tension values of three plant surfactants Reetha, Acacia and Shikakai solutions versus logarithm of concentrations are presented in Figure 6.2. The Figure depicts the solution behavior with the increasing concentrations are similar type for all three plant surfactants studied here. The surface tension value decreases from 71.5 mN/m (pure water) to a minimum value near to CMC of all three surfactants. Minimum surface tension values achieved are 38.29 mN/m (at 0.513 mM), 43.56 mN/m (at 0.389 mM), and 38.71 mN/m (at 0.5 mM) for Reetha, Acacia, and Shikakai respectively.

These surface tension values are significantly higher than the conventionally used single-chain cationic (CTAB = 32.99 mN/m), anionic (SDBS = 34.22 mN/m) (Ghosh Chaudhuri and Paria, 2009), and nonionic (TX-100 = 31.01 mN/m, Igepal CO-630 = 31.02 mN/m) (Biswal and Paria, 2011) surfactants for several applications. The surface excess concentration at air-water interface and area occupied per molecule for Reetha, Acacia and Shikakai were also calculated by Gibbs adsorption equation (4.5) using the surface tension data below the CMC region.

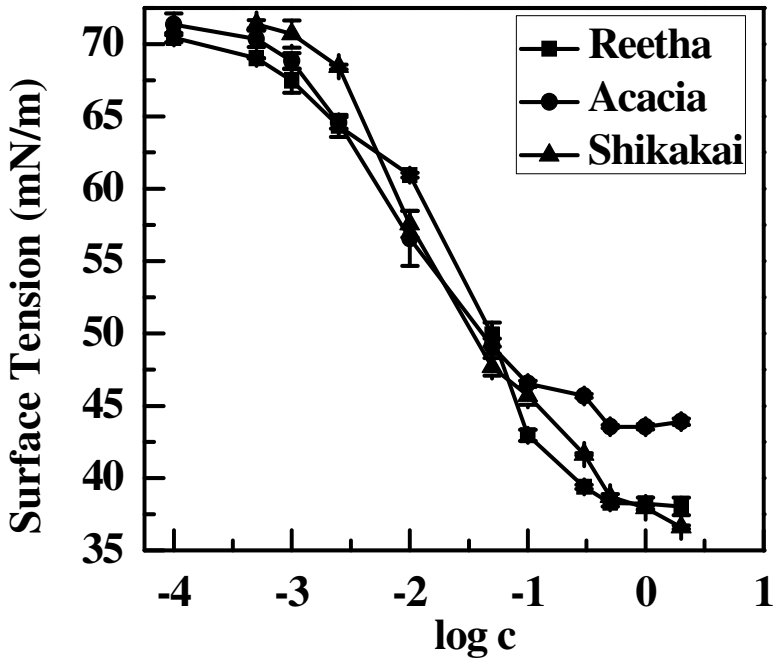


Figure 6.2. The change in surface tension (mN/m) with the concentration (log c) of different surfactants.

The values obtained are shown in Table-1. It can be seen that the area occupied by Reetha and Shikakai are very close and the values are lower than Acacia. The results indicate lower surface tension values for Reetha and Shikakai than Acacia is mainly because of the closer packing of the surfactant molecules at air-water interface.

Table 6.1 CMC, Surface tension at the CMC, Surface excess, and area occupied per molecule at air-water Interface for Reetha, Acacia and Shikakai.

Surfactant	CMC (mM)	γ_{CMC} (mN/m)	Γ_{LG} (mmol/m^2 x 10^6)	A_{min} (Å^2)
Reetha	0.52	38.29	1.70	97.48
Acacia	0.39	43.56	1.54	107.23
Shikakai	0.50	38.71	1.71	97.02

6.3.3 Adsorption of Plant Surfactants on PTFE Surface

Adsorption kinetics of three different plant based surfactants Reetha, Shikakai, and Acacia from 0.05 mM initial concentration at PTFE–water interface are presented in Figure 6.3. The adsorption kinetics was studied mainly to know the equilibrium time for the adsorption process.

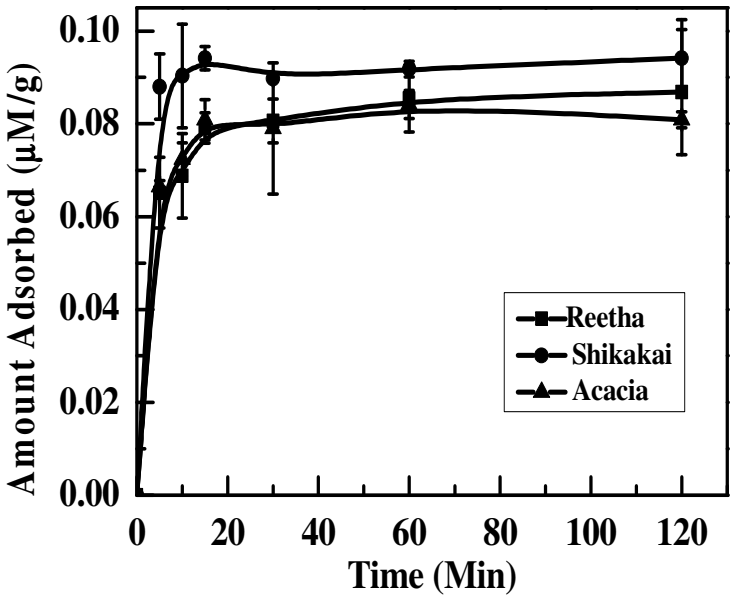


Figure 6.3. Adsorption kinetics at 0.05 mM concentration of Reetha, Shikakai and Acacia surfactants on the PTFE powder.

The Figure shows that equilibrium times for all the three surfactants are close to 15 min, with a slight higher adsorption capasity for Shikakai. After knowing the equilibrium time, adsorption isothem was also studied for all three surfactants to know the maximum adsorption capasity.

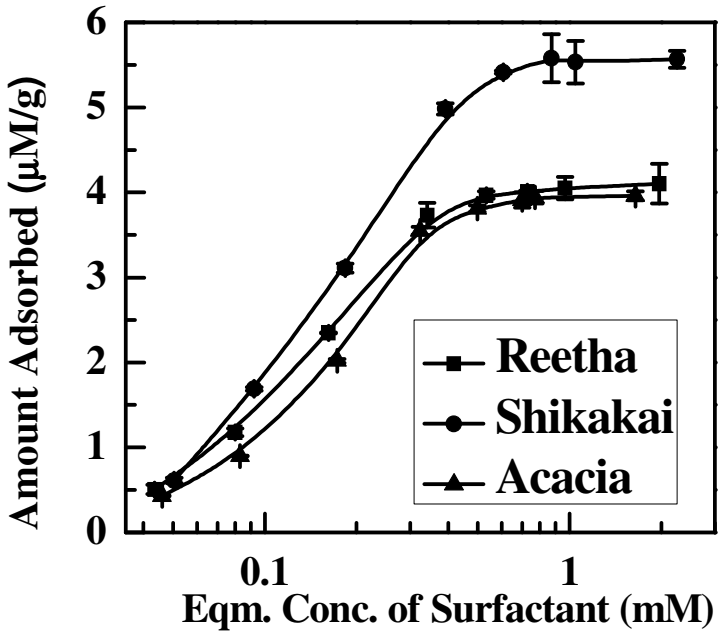


Figure 6.4. Adsorption isotherms of Reetha, Shikakai and Acacia on PTFE powder

Figure 4 depicts the adsorption isotherms of three plant surfactants on the PTFE surface. From the Figure 6.4 it is clear that the nature of the isotherms are similar with different amount adsorbed, also noteworthy to mention that for all three cases adsorption amount is significantly low (in the range of μM/g). While comparing isothemrs of Reetha and Acacia, they are almost close to each other with a little higher adsorption for Reetha, however there is a distinct difference with Shikakai which is having higher adsorption density. The plateau level adsorption occurs just above the CMC for all three surfactants.

There are several models available in literature to fit the adsorption isotherms to know the isotherm type; however the nature of adsorption isotherms reported here are very simple. That reason we tried to fit the isotherms with two types of simple models, Langmuir and Freundlich isotherms which are widely used in many adsorption studies at solid-liquid interfaces given in equations (3.8) and (3.9).

When the interaction between the adsorbate molecules and surface is predominant but the intermolecular interaction between the adsorbed surfactant molecules is negligible, adsorbate forms a monolayer preferably and then Langmuir model works quite well. The Langmuir and Freundlich adsorption constants and the correlation coefficients (R^2) are calculated from the fitting of experimental data with equations (3.8) and (3.9) and listed in Table 6.2.

From the Table 6.2, it is clear that all the three plant surfactants are fitting better with Langmuir isotherm model and forming a monolayer on the PTFE surface probably by adsorbing through the tailgroup on the surface. Initially the adsorption density increases almost linearly with the equlibrium concentration *i.e*. follows Henry's law and ultimately reaches to a plateaue region.The values of *b* decreases for three surfactants in the following order: Shikakai > Reetha > Acacia.

Table 6.2. Parameters of Langmuir and Freundlich isotherm equations.

Surfactant	Langmuir			Freundlich		
	q_m ($\mu M\ g^{-1}$)	$b \times 10^{-3}$ (mM^{-1})	R^2	a ($\mu M\ g^{-1}$)	n	R^2
Reetha	4.651	0.122	0.978	4.466	1.862	0.815
Shikakai	6.41	0.188	0.969	5.714	1.795	0.804
Acacia	4.926	0.091	0.94	5.714	1.55	0.85

From the maximum adsorption capacity, the molecular density or the adsorption density of the surfactants can be expressed in terms of the effective area occupied per surfactant molecule at the PTFE-water interface. Assuming that monolayer adsorption occurs at the PTFE-water interface area, the area occupied per molecule and surface excess concentration can be calculated by equation (4.5) and (4.6)

The values for the area occupied per molecule obtained from the above equations for Reetha, Acacia and Shikakai are 155, 146, and 112 $Å^2$ respectively. The values obtained clearly indicate that the adsorption densities of respective surfactants are less than that of air liquid interface. While comparing area per molecule at air-water and PTFE-water interfaces, it can be observed that at PTFE-water interface adsorption densities of Reetha, Acacia, and Shikakai are 0.628, 0.734, 0.866 times respectively that of air-water interface.

6.3.4 Wettability of Plant Surfactants Solutions on PTFE Surfaces

The advancing contact angle using three plant surfactants solutions on the PTFE surface are presented in Figure 5. Figure depicts that there is a decrease in contact angle with the increase in surfactant concentration until CMC for all three surfactants and above that it is almost constant. Similar to the adsorption study, Reetha and Acacia show very close change in contact

angle with the increasing concentrations, whereas Shikakai shows much lower contact angle values compare to other two surfactants.

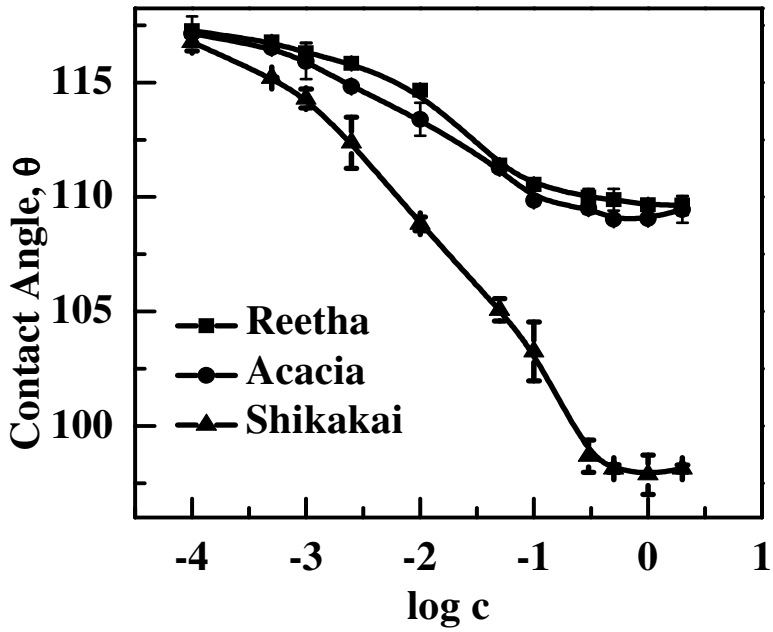


Figure 6.5 Relationship between the values of contact angle, (θ) and concentration (log c) of different surfactants.

The plateau level contact angle values for Reetha, Acacia, and Shikakai are 109.88°, 109.02° and 98.13° respectively compared to 116.5° for pure water. Lower contact angle by Shikakai solutions indicate better wetting ability than the other two plant surfactants may be because of higher adsorption ability on PTFE-water and air-water interfaces as mentioned before.

Additionally, just to get an idea about the surface activity of these surfactants contact angle values on PTFE surface are compared with the conventionally used some common surfactants. It can be clearly observed that these plant surfactants have inferior wettability compared to different synthetic surfactants such as cationic (CTAB = 84.06°), anionic (SDBS = 86.76°) (Chaudhuri and Paria, 2009), and nonionic (TX-100 = 81.08°, Igepal CO-630 = 83.33°) (Biswal and Paria, 2011). However, much lower contact angle values can also be obtained using double-chain cationic (DDAB = 79) and anionic (AOT = 78.5°) synthetic surfactants (Biswal and Paria 2012).

6.3.5 Comparison of Adsorption Density at PTFE–Water and Water–Air Interfaces

Adsorption densities of surfactants at air-water and solid-water interfaces are an important parameter to change the surface tension or contact angle at the respective interfaces. Adsorption densities at both interfaces are highly possible to measure independently at equilibrium condition as presented in the previous sections. However, from the contact angle studies a comparison of adsorption densities at both the interfaces can also be calculated indirectly under the same dynamic condition by combining Young's and Gibbs equations as presented in equation (4.9). Assuming surface excess of surfactants at PTFE- air interface is zero ($\Gamma_{SA} \approx 0$), equation (6) can be reduced to a linear form, where the ratio of Γ_{SW} to Γ_{AW} can be calculated by plotting $\gamma_{AW} \cos\theta$ versus γ_{AW}.

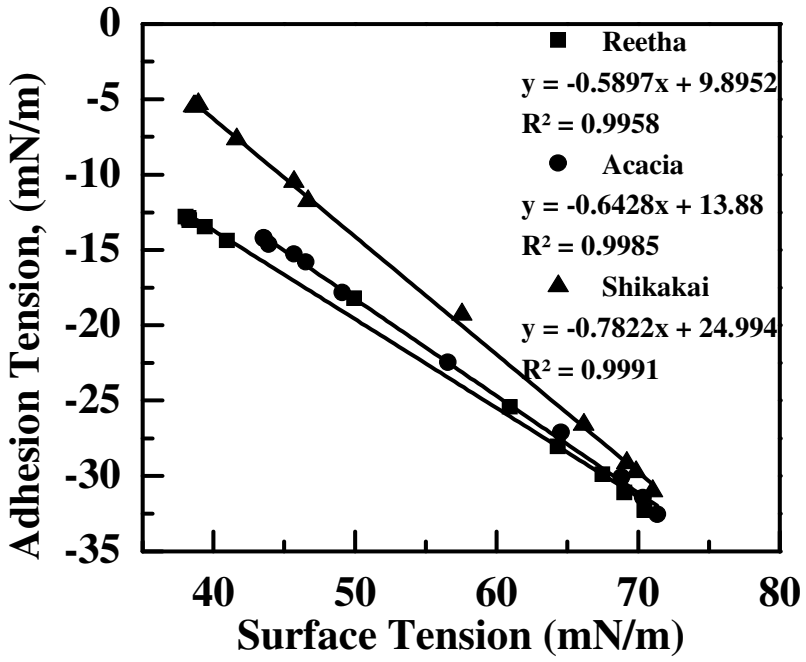


Figure 6.6 Relationship between the values of surface tension (mN/m) and Adhesion tension (mN/m) of different surfactants.

From the Figure 6.6, it can be seen that there is a linear relationship exists between the surface (γ_{LG}) and adhesion ($\gamma_{LG} \cos\theta$) tensions for all the three surfactants with different slope and intersection; for all the three cases the value of slope < 1 indicate unequal adsorption at PTFE-water and air-water interfaces, with a lower adsorption density at PTFE-water interface. The negative slopes for Reetha, Acacia, and Shikakai are 0.589, 0.642, and 0.782 respectively.

These values are lower to that calculated from the ratio of adsorption studies in section 3.3; this can be attributes to lower contact time (~ 25 s) of PTFE and surfactant solutions during the dynamic contact angle measurements.

6.3.6 Work of Adhesion of Surfactant Solution to PTFE Surface

Taking into account equation (4.10) and (4.11), the measured values of the contact angles for aqueous solutions of surfactants on PTFE surfaces and the data of their surface tension, the values of the work of adhesion of solutions to the PTFE surface were calculated, and they are presented in Figure 6.7.

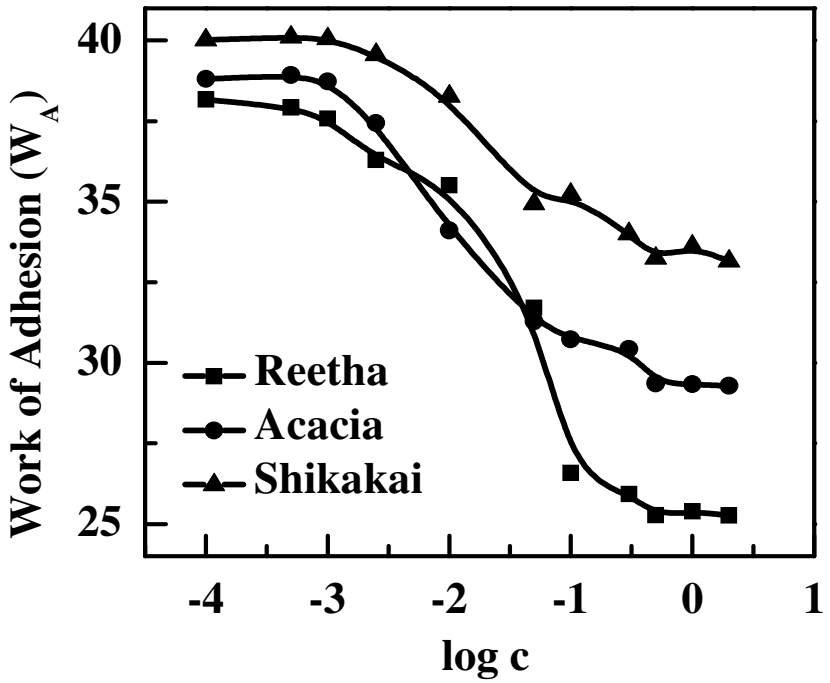


Figure 6.7 Relationship between the values of Work of adhesion (W_A) and Concentration (log c) of different surfactants.

From this Figure, it can be seen that the values of the work of adhesion (W_A) depend on the concentrations of surfactants in aqueous solution and they are in the range of 40-25 mJ/m^2. The final works of adhesion values for Reetha, Acacia, and Shiakaki are 25.26, 30.43, and 33.23 mJ/m^2 respectively. As work of adhesion for Shikakai is highest shows better wettability.

6.3.7 Wetting Free Energy of PTFE from Contact Angles

During the wetting process of PTFE surface in the presence of surfactant solutions, the surfactant molecules are adsorb on the PTFE surface and make it hydrophilic, as a result surface energy increases. In this process, the knowledge of the change in wetting free energy is very important to get an idea about the spontaneity of the wetting; the larger values of the negative wetting free

energy are expected to enhance the wetting process. From the thermodynamic point of view, the molar wetting free energy of the solid can be calculated using the contact angle values (Extrand, 2003) as given in equation (4.14)

The calculated values show the wetting free energy (ΔG) is negative over the total concentration range studied here, indicates the process is spontaneous. There is a decrease in wetting free energy with the increasing surfactant concentration, which is consistent with the increasing contact angle values as mentioned before. The wetting free energies of different surfactants (ΔG) on PTFE surface are -242.838 J/mol; -247.37 J/mol, and -414.44 J/mol for Reetha, Acacia, and Shikakai respectively, which are more negative than pure water (-171.5 J/mol).

6.3.8 Effect of Alcohols on Shikakai Solutions

Surfactants are used in many applications in the presence of additives such as salt, alcohol, a second surfactant and so on to enhance the performance of pure surfactant. Electrolytes are used as additive in the presence of ionic surfactants. As plant surfactants are mostly non-ionic in nature, electrolyte effect was not studied. As pure natural surfactants are inferior with respect to that of synthetic surfactants, effect of two different alcohols was studied to see the possibility of enhancement of wetting property. Further, alcohol effect was studied only on Shikakai as it acts as a better wetting agent among the three plant surfactants studied here. Two different alcohols of straight chain hydrocarbon (C_1: Methanol, C_5: Amyl alcohol) were studied here.

6.3.8.1 Effect of Alcohols on Surface Tension

The changes in surface tension as a function of alcohol concentrations at different fixed Shikakai concentrations are presented in (a) and (b) parts of Figure 6.8 for methanol and amyl alcohol respectively. Both Figures show that there is a gradual decrease in surface tension with the increasing concentration for pure alcohols, but the concentration of alcohol required to reduce similar surface tension for amyl alcohol is almost 10^4 times lower than methanol. More specifically, the surface tension values of 39.82 and 39.45 mN/m were achieved using 1 mM and 10 M of amyl alcohol and methanol solutions respectively. Figure 6.8 (a) shows in the presence of low surfactant concentration (0.001 mM) the change in surface tension is similar to that of pure methanol solution; however with the increasing surfactant concentration surface tension values gradually decreases. The surface tension plots show at low alcohol concentration surface tension changes slowly and above a particular alcohol concentration there is a sharp decrease in surface tension that particular alcohol concentration is dependent on the surfactant concentration,

which gradually increases with the increasing surfactant concentration. That particular point is shown by an arrow mark on the respective curves for both alcohols. Additionally, the slope of lower alcohol concentration region decreases gradually with the increasing surfactant concentration. Similar behavior is also seen for amyl alcohol (Figure 6.8 b), but the concentration of alcohol required is much lower than methanol.

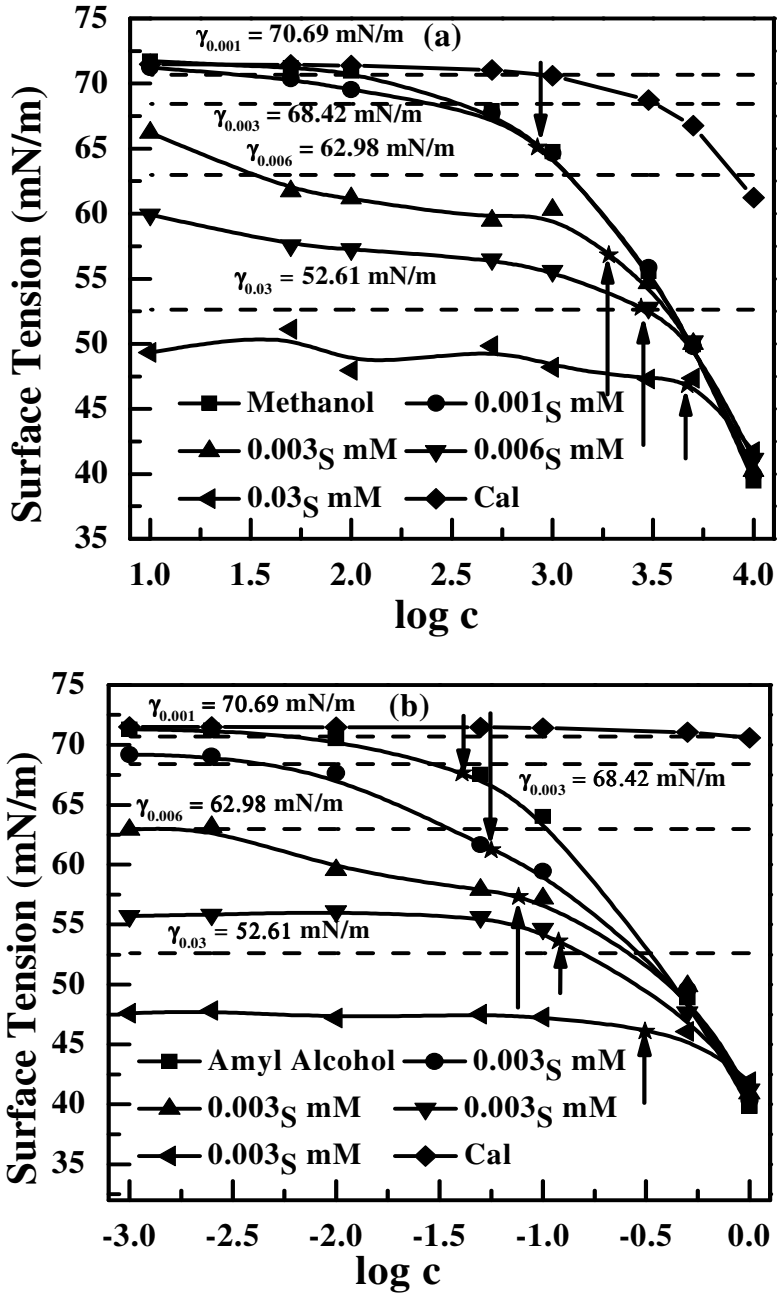


Figure 6.8. Relationship between the alcohol concentration (log c) and surface tension (mN/m) in the presence of constant Shikakai concentration (a) Methanol, (b) Amyl alcohol.

In case of surfactant and alcohol mixture it is very much essential to know whether the solutions behave ideally or non-ideally because of interaction between the surfactant and alcohol molecules. Surface tension of pure water-alcohol mixtures can be calculated ideally assuming a linear function of a surface layer mole fraction

$$\gamma_{w\text{-}a} = \alpha_w \gamma_w + \alpha_a \gamma_a \qquad (6.1)$$

Where $\gamma_{w\text{-}a}$, γ_w, γ_a are surface tensions of water-alcohol mixture, pure water, pure alcohol respectively; and α_w, α_a are mole fraction of water and alcohol in the mixture respectively. It can be seen from Figures 6.8 (a) and (b) that there are deviations between the calculated surface tension values with the experimental one for alcohol-water solutions, and deviations are more in case of amyl alcohol, because of surface excess of the alcohol molecules at air-water interface; which is more for amyl alcohol. When surfactant-alcohol mixture is used, until a certain concentration of alcohol surface tension of water-alcohol solutions and pure surfactant are higher than surfactant-alcohol mixtures. Surface tensions of fixed concentration pure surfactant solutions are shown as dotted lines in Figures (6.8 a, b). If surfactant-alcohol mixtures behave ideally surface tension should be constant up to the alcohol concentration where the pure surfactant and water-alcohol surface tension lines intersect. However, all surfactant-alcohol mixtures show lower surface tension than the expected indicated there is a synergistic interaction between the alcohol and surfactant. The deviation of surface tension from the expected value up to the intersection point in % is calculated as

$$D = \frac{(\gamma_{a-s\,mix} - \gamma_s)}{\gamma_s} \times 100 \qquad (6.2)$$

Where $\gamma_{a\text{-}s\ mix}$ and γ_s are the surface tension values of alcohol-surfactant mixtures and surfactant solutions respectively. If the deviation is negative, indicates synergistic behavior and zero for ideal. When the alcohol concentration is beyond the intersection point then the deviation can be calculated as

$$D = \frac{[\gamma_{a-s\,mix} - (\alpha_a \gamma_{w-a\,\exp} + \alpha_s \gamma_s)]}{(\alpha_a \gamma_{w-a\,\exp} + \alpha_s \gamma_s)} \times 100 \qquad (6.3)$$

Where α_s is the mole fraction of surfactant, $\gamma_{w\text{-}a\ exp}$ is the experimental surface tension of water-alcohol mixture.

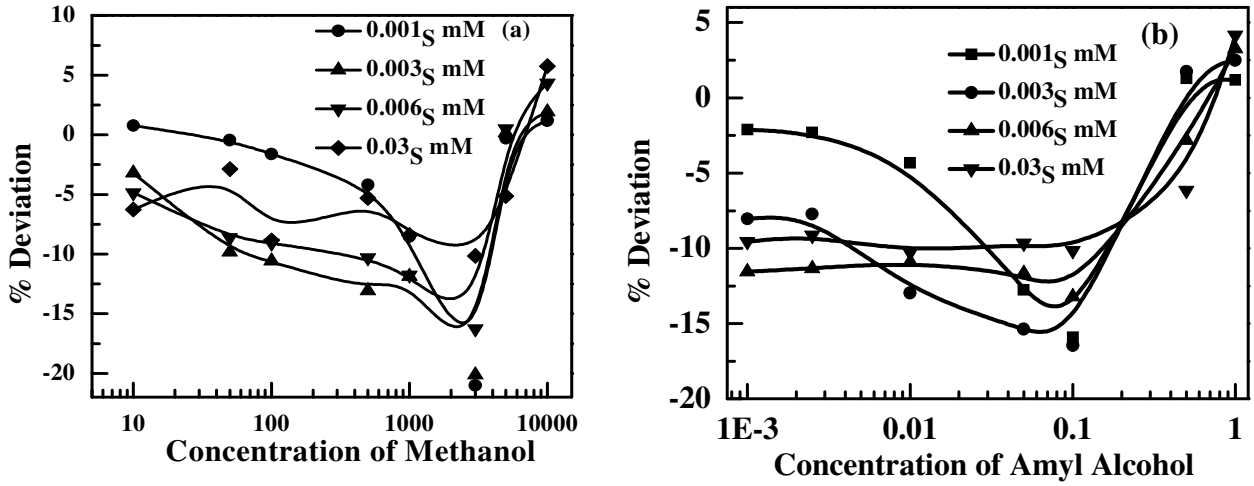


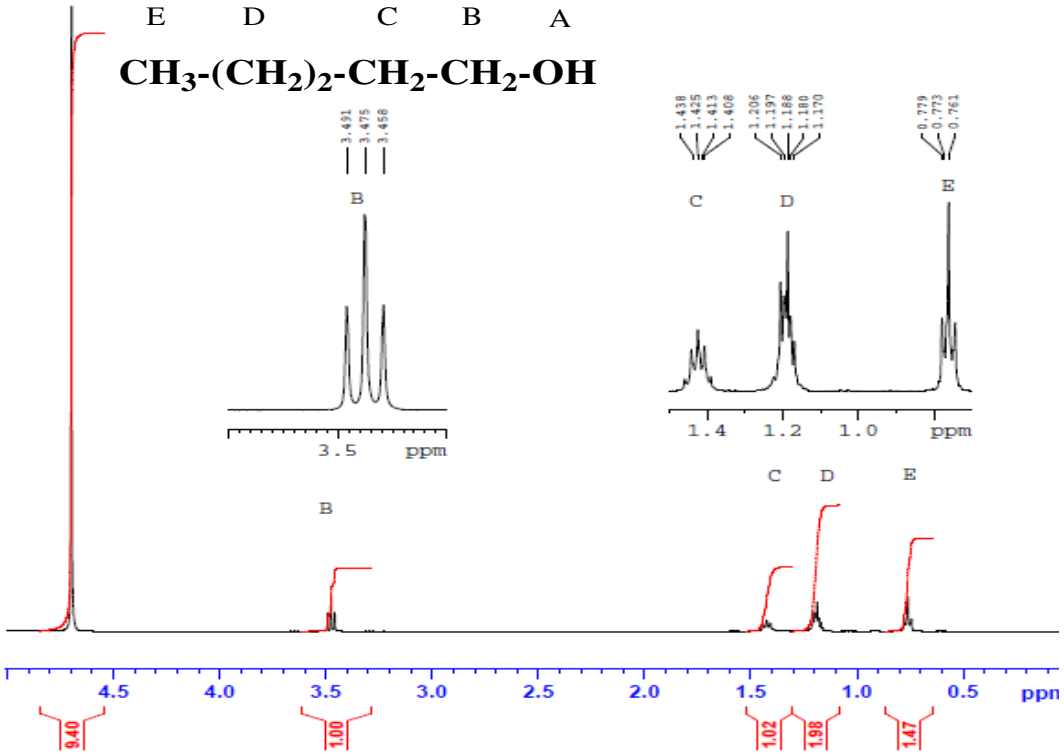
Figure 6.9. Relationship between the values of concentration and % deviation with varying alcohol concentration of (a) Methanol, (b) Amyl alcohol.

Figures 6.9 (a) and (b) show the negative deviations of surface tension increases with the increasing alcohol concentration and after a maximum value of negative deviation, when the alcohol concentration increases further the negative deviation decreases towards zero. This behavior is attributed to the predominance of alcohol effect at very high alcohol concentration. Whereas, at low alcohol concentration because of the interaction between alcohol and surfactant molecules there is a sudden decrease in surface tension and also gradually decreases with the increasing alcohol concentration as more molecules interact with the surfactant molecules. However, as the concentration of surfactant is constant in the solution, after a certain alcohol concentration there would be no free surfactant molecules available to interact with alcohol, maximum deviation occur at that point; beyond that concentration surface tension of alcohol predominates in the mixture.

6.3.8.2 ^{1}H-NMR measurements of alcohol-shikakai mixture.

The interaction between Shikakai and alcohol was further supported by ^{1}H-NMR spectra measurements in D_2O. ^{1}H NMR spectra of pure amyl alcohol, and their mixture of amyl alcohol-Shikakai at 50:50 molar ratio in D_2O are represented in (a) and (b) parts of Figure 6.10 respectively.

(a)



(b)

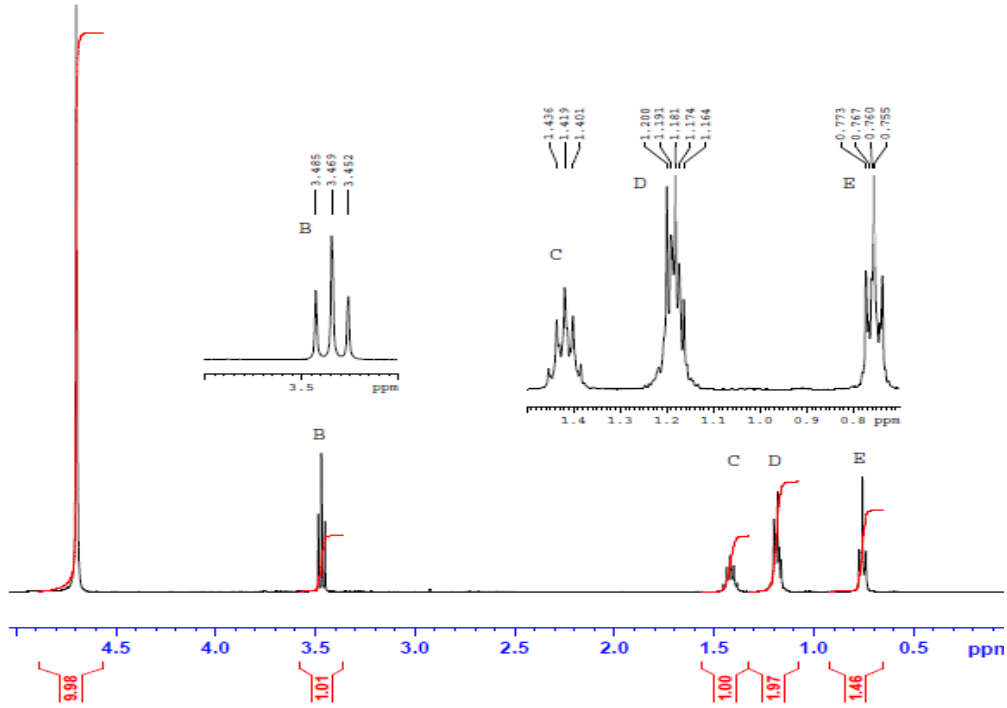


Figure 6.10: (a) Labelled structure of amyl alcohol, (b) ^{1}H NMR spectrum of amyl alcohol. (c) ^{1}H NMR spectrum of Shikakai – amyl alcohol mixture at 50:50 molar ratio.

The various protons attached to carbon atoms are labelled on the structure of amyl alcohol and the chemical shift δ (ppm) values are presented in Table 6.3. The ^{1}H NMR peaks of protons attached to different carbon atoms of amyl alcohol are marked from letter A to F and their corresponding δ values are identified. A triplet for protons attached to carbon B (δ_{CH_2}) = 3.458-3.491 ppm, multiplets for C (δ_{CH_2}) in the range of 1.408-1.442 ppm and D (δ_{CH_2}) in the range of 1.170-1.206 ppm, and a triplet for E (δ_{CH_2}) in the range of 0.761-0.799 ppm are because of three protons. The absence of A peak can be attributed as rapid OH exchange with the deuterium of D_2O (ROH + D_2O ⇆ ROD + D-O-H). To get some idea about the interaction between alcohol and Shikakai, ^{1}H NMR spectra of the mixture (1:1 molar ratio) are compared with pure alcohol. The mixed solution shows upfield shifting (towards right) of spectra for all protons of amyl alcohol presented in Table 6.3, which support interaction between amyl alcohol and shikakai.

Table 6.3: ^{1}H-NMR peak positions for pure amyl alcohol and amyl alcohol-Shikakai mixture.

Peaks	B	C	D	E
δ_{AA} (ppm)	3.458, 3.475, 3.491	1.413, 1.425, 1.438	1.170, 1.180, 1.188, 1.197, 1.206	0.761, 0.773, 0.799
δ_{Mix} (ppm)	3.452, 3.469, 3.485	1.401, 1.419, 1.436	1.164, 1.174, 1.181, 1.191, 1.200	0.755, 0.760, 0.773

6.3.8.3 Surface Excess of Amyl Alcohol and Methanol with Varying Shikakai Concentration

Surface excess of surface active solute molecules at air-liquid interface is directly related to adsorption density, which in turn controls the surface tension of the liquid. The surface excess (Γ) of the surfactant and alcohols can be calculated from the plot of surface tension as a function of alcohol and surfactant concentrations using the Gibbs adsorption equation (6.4 and 6.5):

$$\Gamma_A = \frac{1}{2.303nRT}\left(\frac{d\gamma_{LG}}{d\log c_A}\right)_{C_S} \quad (6.4)$$

$$\Gamma_S = \frac{1}{2.303nRT}\left(\frac{d\gamma_{LG}}{d\log c_S}\right)_{C_A} \quad (6.5)$$

where n is a constant equal to one for nonionic surfactant, subscripts A and S are used for alcohol and surfactant respectively, c is the concentration, R is gas constant (8.31 J/mol^{-1}K^{-1}), T is absolute temperature (298K),

From the surface excess values the area occupied per surfactant molecule (A_{min}) at air-water interface in Å^2 can be calculated from the equation (4.5):

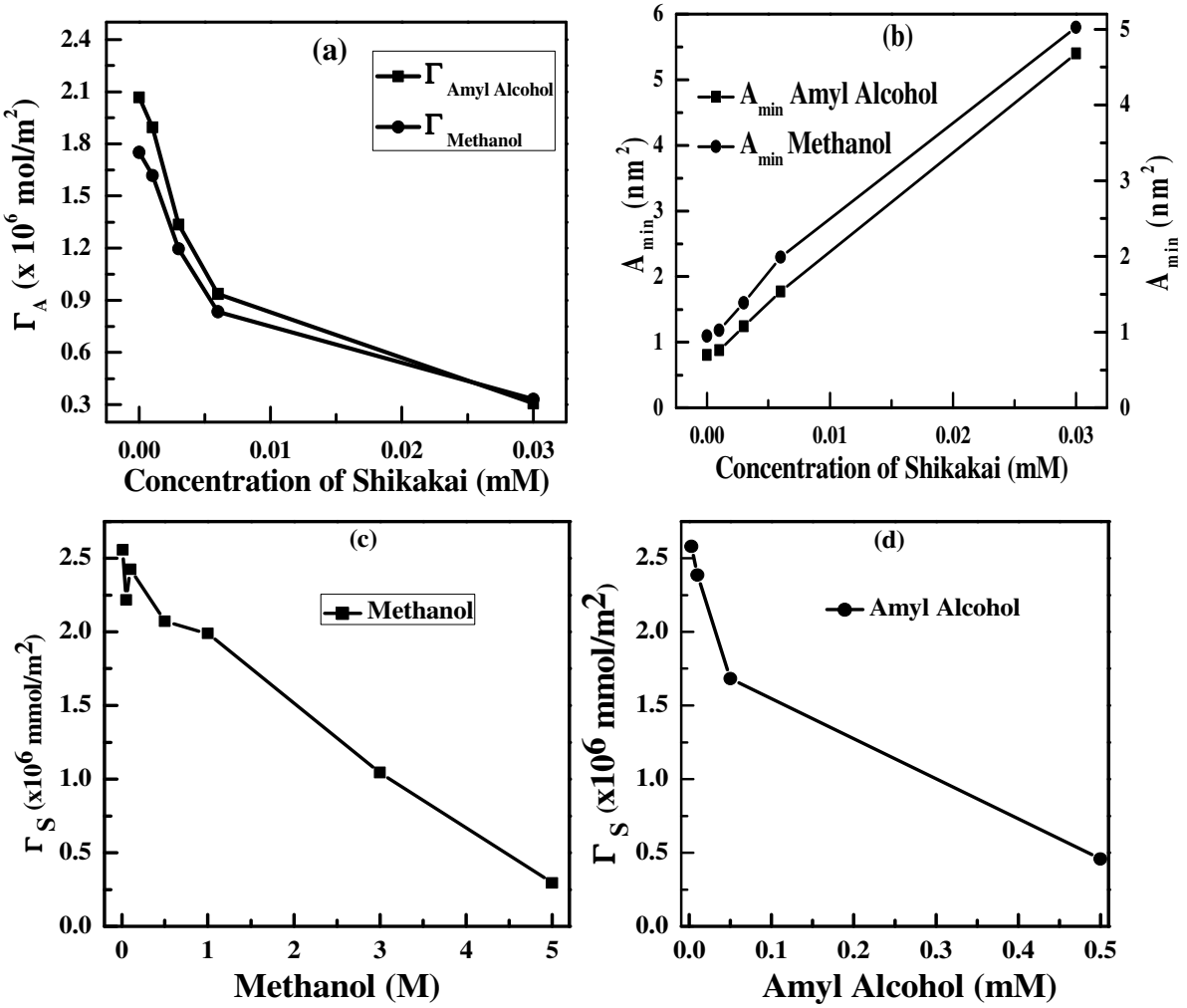


Figure 6.11 Relationship between the values of (a) surface excess of Methanol and Amyl alcohol, (b) area per molecule with varying Shikakai concentration, surface excess of shikakai with varying (c) Methanol (d) Amyl alcohol concentration.

The changes of surface excess concentration of alcohols at air-water interface and area per molecule as a function of Shikakai concentration in the bulk phase presented in Figure 6.11 (a, b). The Figure depicts surface excess of both alcohols decreases sharply with the increasing surfactant concentration may be because of higher surface activity of surfactant than the

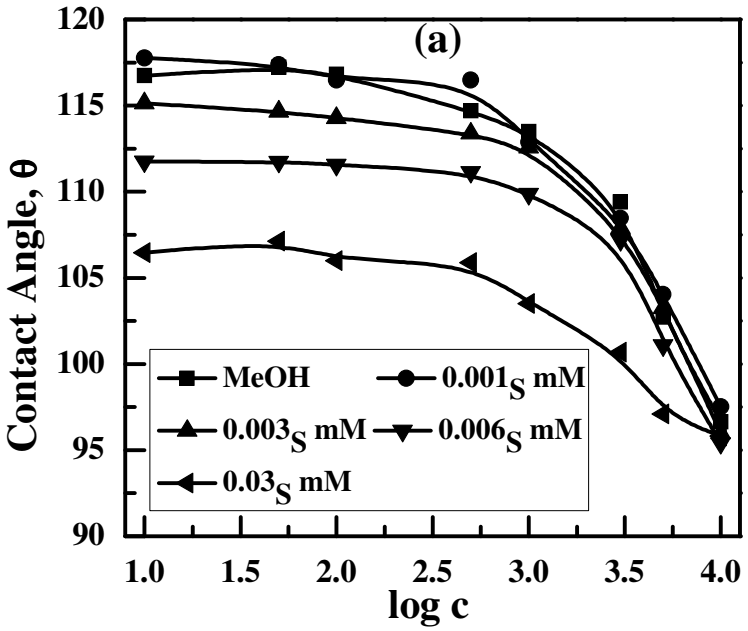
alcohols. As a result, area occupied per molecule of alcohol also increases linearly with the increasing surfactant concentration.

The changes of surface excess concentration of surfactant at air-water interface as a function of alcohol concentration presented in Figure 6.11 (c, d). From the Figures it is clear that the surface excess concentration of Shikakai decreases with respect to total surface excess as that of alcohol increases with the increase in alcohol concentration.

6.3.8.4 Wetting of PTFE Surface by Shikakai–Alcohol Mixtures

Similar to the surface tension study contact angle measurements were done using same solutions and the contact angle values are plotted in parts a and b of Figure 6.12 for methanol and amyl alcohol respectively. It has been found that changes in contact angle values are very much similar to the surface tension results.

In case of pure alcohol-water mixture the contact angle reduces from pure water to 96.65º and 98.09º in the presence of 10 M and 1 mM for methanol and amyl alcohol solutions respectively. For both alcohols in the presence of low surfactant concentration (0.001 mM) the change in contact angle is similar to that of pure alcohol solutions; however with the increasing surfactant concentration gradually contact angle decreases. For shikakai-alcohol mixture at lower alcohol concentration reduction in contact angle is more with respect to pure alcohol-water mixtures may be because of synergistic interaction as mentioned before. These results indicate addition of alcohol improve the wettability of natural surfactant because of the synergistic effect.



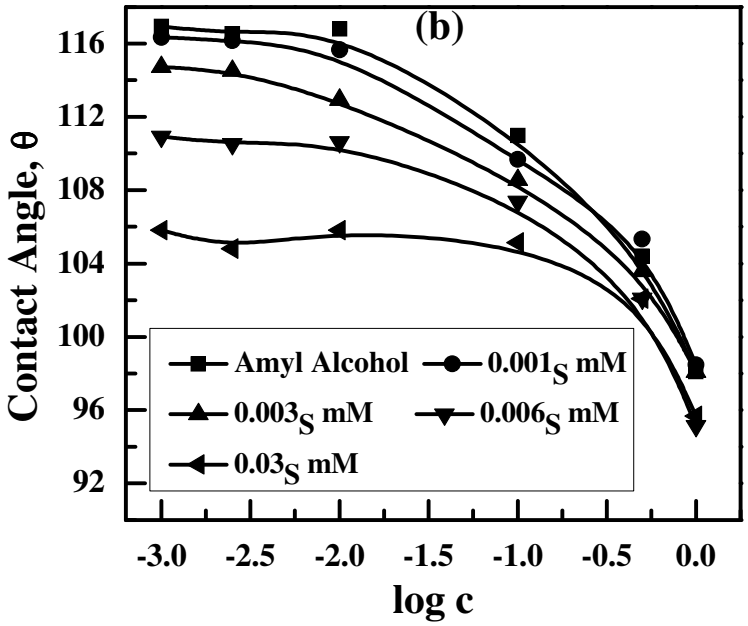


Figure 6.12 Relationship between the values of concentration (log c) of and change in contact angle of (a) Methanol, (b) Amyl alcohol with varying different Shikakai concentration.

6.4 Conclusions

The surface tension measurements show surface tensions at CMC for Reetha and Shikakai are very close (~ 38.3 mN/m) but little higher for Acacia (~ 43.6 mN/m), which in turn show surface excess values at air-water interface for Reetha and Shikakai are higher than Acacia. The adsorption kinetics of these surfactants on PTFE surface show adsorption comparatively fast and approximately within ~20 minutes equilibrium reaches. A Langmuir-type isotherm fits well for all three surfactants studied here. The maximum adsorption capacities of three surfactants at PTFE-water interface are found to be in the following order: Shikakai > Reetha ≈ Acacia. The comparisons of area per molecule at air-water and PTFE-water interfaces show that at PTFE-water interface adsorption densities of Reetha, Acacia, and Shikakai are 0.628, 0.734, 0.866 times less respectively than that of air-water interface. The change in contact angle on PTFE surface by the surfactant solutions also follow similar trend to that of adsorption density; for Reetha, Acacia, and Shikakai are 109.88°, 109.02° and 98.13° respectively. The contact angle studies also independently support lower adsorption density at PTFE-water interface than air-water interface for all three surfactants.

The addition of methanol and amyl alcohol to the Shikakai solution show there is a synergistic interaction between the alcohol and Shikakai molecules and that is more for amyl alcohol. Since

the interaction is more for amyl alcohol consumption of alcohol is also 1000 times lower than methanol to get similar surface tension reduction. When the concentration of Shikakai is constant with the increasing concentration of alcohols up to a certain concentration of alcohol reductions in surface tension and contact angle are more than that of pure solutions of similar concentrations because of synergistic interaction.

Chapter 7

Wetting of glass surface using natural surfactants

Chapter 7

Wetting of glass surface using natural surfactants

7.1 Introduction

Surfactant adsorption at the interfaces (solid–liquid, liquid–air, or liquid–liquid) is receiving considerable attention for long time due to its wide range of practical applications in many processes like wetting of solid surfaces and detergency (Janczuk and Chibowski, 1985), dispersion and colloid stability (Prez-Arvalo et al., 2002; Blin et al., 2001), remediation of organic contaminants (Rao and Paria, 2009), flotation (Danis and Aydiner, 2009), agriculture (Boopathy, 2002), and so on. Specifically wettability of solid surface by liquids is mainly measured by contact angle and has many practical importance's where solid–liquid systems are used. Adsorption of surfactants plays an important role in the wetting process. The wettability of solid surfaces by aqueous surfactant solutions depends on liquid–air, solid–air, and solid–liquid interfacial tensions (Rosen, 2004; Adamson and Gast, 1990), also can be explained from the Young's equation. It is well known that addition of surfactants in aqueous medium always decreases water–air interfacial tension due to adsorption of surfactants, more adsorption at the interface more decrease in interfacial tension. Whereas, for solid–interface the presence of surfactants may increase or decrease the interfacial tension depends on surface properties of solids as well as the nature of adsorption.

In view of the widespread applications of wetting phenomena many researchers have studied the wettability of different types of flat solid surfaces like hydrophilic glass (Szymczyk and Janczuk, 2008), quartz (Zdziennicka et al, 2009; Zhang, et al. 2010) and mica (Pashley and Israelachvili, 1981), hydrophobic PTFE and semi-polar polymethyl methacrylate surface (Chaudhuri and Paria, 2009; Szymczyk et al., 2006) using single surfactants (Pashley and Israelachvili, 1981; Janczuk et al., 1997), mixture of two cationic (Szymczyk, et al., 2006), two nonionic (Szymczyk and Janczuk, 2007; Szymczyk and Janczuk, 2008), mixture of both cationic and nonionic surfactant (Szymczyk and Janczuk, 2006), and also most recently mixture of surfactant and co-surfactants (Zdziennicka et al., 2005; Zdziennicka and Janczuk, 2008a, b; Zdziennicka, 2008, 2009; Zdziennicka and Janczuk, 2010). Pashley and Israelachvili (1981) found that there is a consistency in adsorption behavior of CTAB on mica with wetting and adhesion properties. Sikalo et al., (2005) have investigated the dynamic contact angle on glass

surface and found the dynamic contact angle is a function of both contact line speed as well as the flow field in the vicinity of the moving contact line. Vogler (1992) shows the concentration dependent contact angle on glass surface in presence of cationic and nonionic surfactants can be interpreted in terms of Gibb's adsorption isotherm. Ozdemir and Malayoglu (2004) have studied the wetting properties of anionic biosurfactants (rhamnolipids) on hydrophilic glass surface and found that at low concentration similar contact angle with SDS but above a certain concentration rhamnolipid shows better wetting at even an order of magnitude lower concentration. The anionic surfactant with two tail groups (AOT) shows there is almost linear relationship between the contact angle and log c under a certain concentration range (Harkot and Janczuk, 2008). The decrease in contact angle in presence of AOT is probably due to decrease in surface tension of aqueous AOT solution rather than adsorption of surfactants at solid – liquid interface. A mixture of two nonionic surfactants (TX-100 and TX-165) shows contrast to previous study, lowest wettability corresponds to the concentration of TX-100, TX-165, and their mixture near the CMC. They have found a linear dependence between the adhesional tension ($\gamma_{LG} \cos \theta$) and surface tension (γ_{LG}) of aqueous solutions of mixed surfactants with a positive slope. For each surfactant and their mixtures the slope is different. Ghzaoui, (1999) shows the increase in contact angle on silica surface in presence of nonionic surfactant (TN 101) well below the CMC due to formation of monolayer and again decreases till around CMC until complete bilayer formation of surfactants on silica surface.

From the literature it is clear that wetting properties on glass or other hydrophilic surfaces have been studied by many researchers using synthetic surfactants and one study with rhamnolipids biosurfactants. Most of the synthetic surfactants are having adverse environmental effect when thrown to the environment after the use due to mainly non-biodegradable nature of the molecules. The surfactants from biological or natural sources are getting more attention recently due to their easy biodegradability and nontoxicity. In this study we have concentrated on the wetting behavior and dynamic contact angles of hydrophilic glass surface using three natural surfactants from plant source. Wetting behavior of these surfactants has not been reported to the best of our knowledge. To compare the results we have also studied one synthetic nonionic surfactant

7.2 Material and Methods

7.2.1 Materials

Same as mentioned in chapter 3 and 4

7.2.2 Methods

7.2.2.1 Dynamic Contact Angles Measurement

The contact angle of the surfactant solutions on PTFE surface were measured according to the method described in chapter 4.

7.3 Results and Discussion

7.3.1 Contact Angle of Surfactant Solutions on Glass Surface

Similar to PTFE surface the advancing contact angle on glass surface was studied using three natural surfactants and one nonionic synthetic surfactant (Triton X-100) as a reference to compare, the results are presented in Figure 7.1. Figure 7.1 depicts that there is an increase in contact angle from 47° (pure water) to 67.72, 65.57, 68.84, and 68.79° for Reetha Acacia, Shikakai, and Triton X-100 respectively at the saturation level with the increase in surfactant concentration. The final contact angle values indicate Reetha and Shikakai are very close to that of TX-100, however Acacia shows ~3° lower contact angle value than the others.

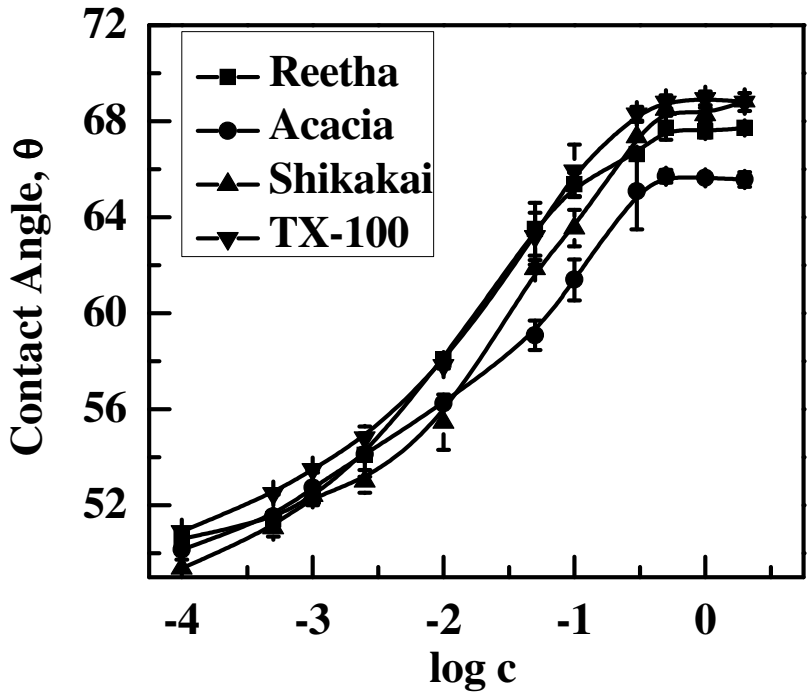


Figure 7.1 The change in contact angle (θ) with the concentration (log c) of different surfactants.

7.3.2 Surface Excess at Glass–Water and Air-Water Interfaces

According to Young's equation, the contact angle on solid surface depends on the surfaces energies of air-liquid and solid–liquid interfaces, which in turn, again depends on the adsorption of the surfactant molecules on both the interfaces when they are present in the liquid phase. The change in surface energy of the interfaces because of the adsorption of surfactant molecules depends on types of molecules, adsorption density, adsorption pattern, and so on. The surface excess at air-water interface can be measured by the help of surface tension measurement, however that at flat solid-water interface is difficult to measure in situ. The measurement of contact angle on the flat surface, on the other hand, can give the surface excess at solid-water interface with respect to that at air-water interface. A relation between the contact angle and surface excess can be developed by combining Lucassen-Reynders (1963; 1966), Young's, and Gibbs equations, as mention in equation (4.9)

For the present study Γ_{SG}, Γ_{SL}, and Γ_{LG} represent the surface excess of surfactants at the glass–air, glass–water, and air–water interfaces respectively. Assuming that surface excess of surfactants at solid- air interface to be zero ($\Gamma_{SG} \approx 0$), the equation can be transformed to a linear form and the plot of $\gamma_{LG} \cos \theta$ (adhesion tension) versus γ_{LG} gives slope (Γ_{SL}/Γ_{LG}) of less than one for each individual surfactants as Shown in Figure 7. 2. This indicates that the surface excess of all four surfactants at glass-water interface is less than that at air-water interface. The individual slopes obtained from the linear fitting in the decreasing order are 0.962, 0.957, 0.909, and 0.824 for Shikakai, Acacia, Reetha, and TX-100 respectively. From the surface tension results it has been found that the decreasing order of surface excess values are 2.36, 2.06, 1.70, 1.51 mM/m^2 for TX-100, Shikakai, Reetha, and Acacia respectively. Now, using these ratios of surface excess at two interfaces (Γ_{SL}/Γ_{LG}) and the surface excess values at air-water interface the surface excess values at glass-water interface are calculated, the surfactant adsorption densities at the glass-water interface in decreasing order are 1.98, 1.94, 1.54, and 1.44 for Shikakai, TX-100, Reetha, and Acacia respectively; which is also consistent with the contact angle results.

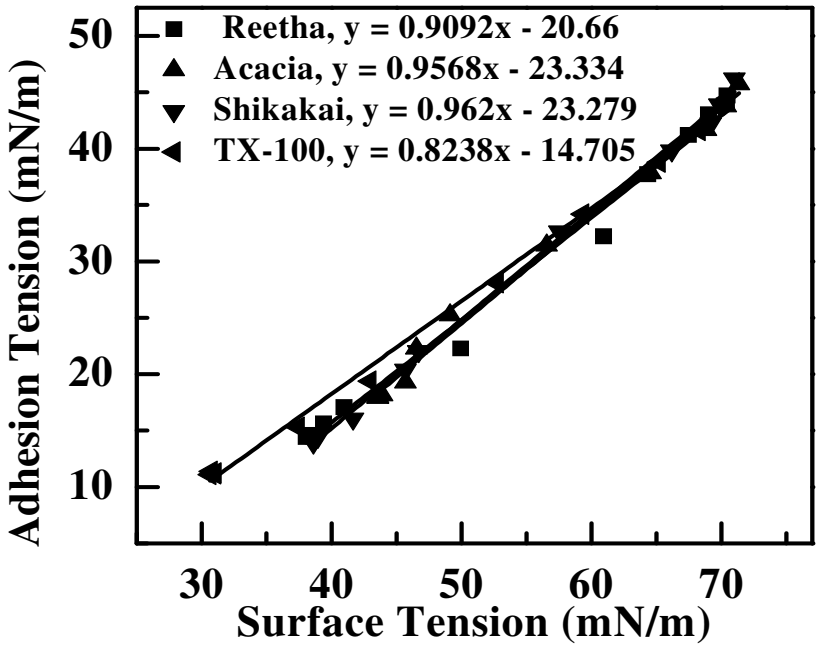


Figure 7.2 The plot of surface tension (mN/m) vs. adhesion tension (mN/m) of different surfactants.

7.3.3 Work of Adhesion of Surfactant Solutions to Glass Surface

The work of adhesion of a liquid on the solid are determined using equation (4.10) and (4.11). The works of adhesion values for different surfactants with increasing concentrations are depicted in Figure 7.3. The figure shows work of adhesion (W_A) for different surfactants depend on the type and concentration of surfactants. The final works of adhesion values for different surfactants are 52.81, 61.48, 52.91, and 41.73 mJ/m^2 for Reetha, Acacia, Shikakai, and Triton X-100 respectively. The work of adhesion of water on glass is 120.71 mJ/m^2. For Triton X-100 the change in work of adhesion is little more than these three natural surfactants.

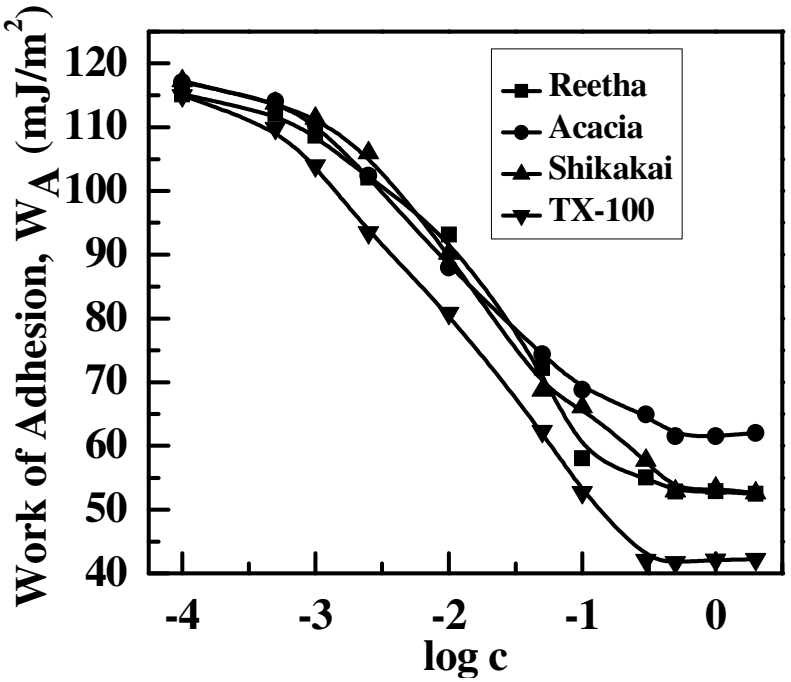


Figure 7.3 The change in work of adhesion (W_A) with surfactant concentration (log c) of different surfactants.

But in case of three plant surfactants work of adhesion of acacia is little more compare to Reetha and Shikakai.

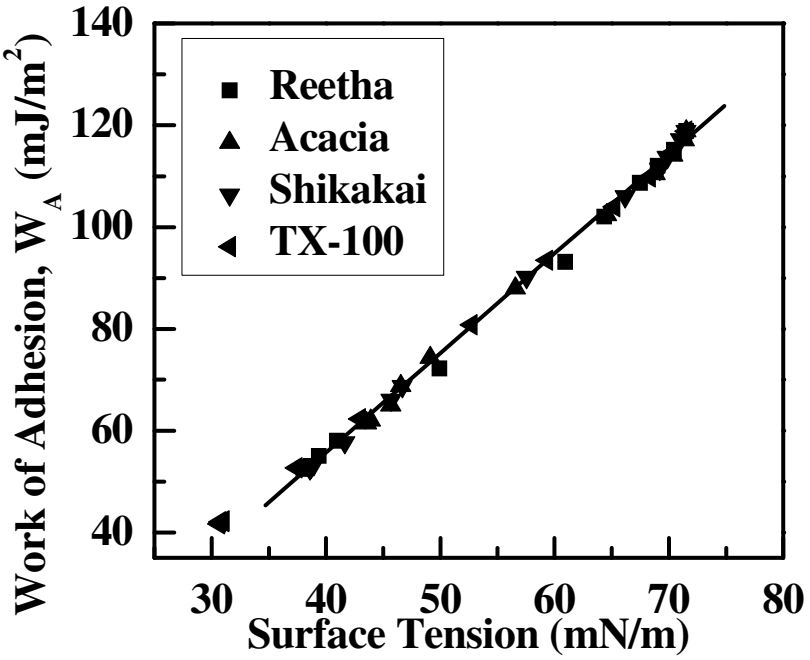


Figure 7.4 Relationship between the values of Work of adhesion (W_A) and Surface tension (mN/m) of different surfactants.

To see the dependency of work of adhesion with surface tension, it has been found from Figure 7.4 that there is a liner relationship, which is independent on the types of surfactants used. The work of adhesion decreases linearly with surface tension of the surfactant solutions, attributed to the higher adsorption density at the glass-water interface, which in turn increases the hydrophobicity of the surface.

7.3.4 Free Energy of Wetting

The surface free energy quantifies the strength of interaction that spread the liquid onto the solid surface. From the thermodynamic point of view the molar wetting free energy of the solid can be calculated according to equation (4.14).

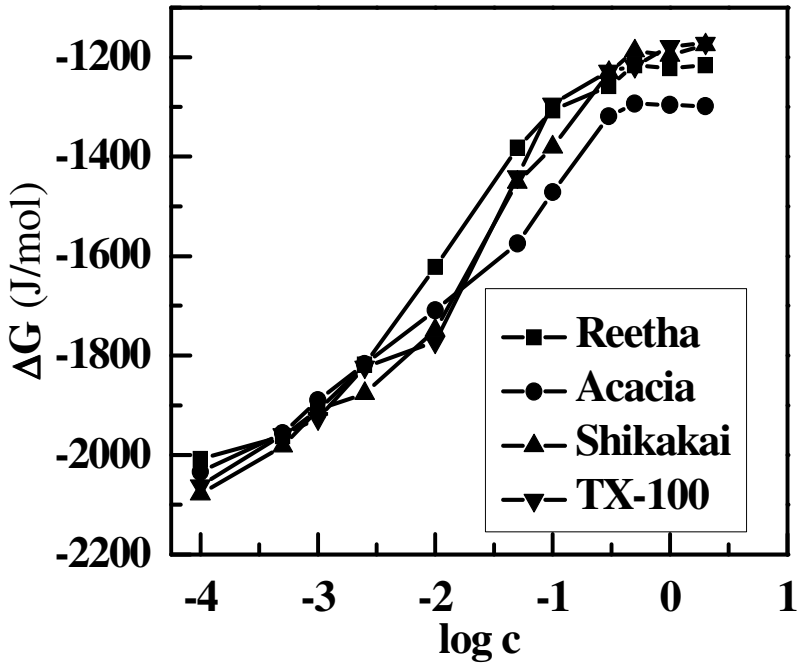


Figure 7.5 The change in surface wetting free energy (ΔG) with concentration (log c) of different surfactants.

The molar wetting free energy calculated by equation (4.14) is presented in Figure 7.5. The figure shows surface wetting free energy (ΔG) is negative over the total concentration range studied here, indicates the process is spontaneous. However, there is an increase in surface free energy with increase in surfactant concentration, consistent with the increasing contact angle values as mentioned before. The wetting free energies of different surfactants (ΔG) on glass surfaces are -1216.23, -1293.40, -1187.73, and -1218.22 J/mol for Reetha, Acacia, Shikakai,

and Triton X 100 respectively, which are again less negative than the pure water (-2253.88 J/mol).

7.3.5 Effect of Alcohols on Shikakai Solutions

Surfactants are used in many applications in the presence of additives such as salt, alcohol, or a second surfactant and so on to enhance the performance of pure surfactant. Electrolytes are used as additive for ionic surfactants. As plant surfactants are mostly non-ionic in nature, electrolyte effect was not studied. As pure natural surfactants are inferior with respect to that of synthetic surfactants, effect of two different alcohols was studied to see the possibility of change in contact angle. Further, alcohol effect was studied specifically on Shikakai similar to that of PTFE surface. Two different alcohols of straight chain hydrocarbon (C_1: Methanol, C_5: Amyl alcohol) were studied here.

7.3.5.1 Effect of Alcohols on Wettability of Glass Surface

The change in contact angle values on the glass surface with respect to increasing alcohol concentrations are presented in (a) and (b) parts of Figure 7.6 for methanol and Amyl alcohol respectively. From both the figures it is clear that there is a gradual increase in contact angle with the increasing concentrations of alcohols in the absence and presence of Shikakai. The increase in contact angle is mainly because of the attachment of alcohols on silica surface through the hydroxyl group. Initially at low the concentration of methanol change in contact angle is less till 1 M, and above that there is a sharp increase in contact angle till 10 M (61.43º). In contrast, for amyl alcohol starting from very low concentration contact angle increases gradually and reaches to a value of 63.33º at 1 mM, which 10^4 times lower than that of methanol. When the Shikakai concentration is low in the presence of methanol and Shikakai mixtures, the change is almost similar to that of pure methanol solutions, however when the concentration of surfactant is 0.003 mM or higher the change is significant. At higher alcohol concentration predominance of alcohol is more, that reason for different alcohol surfactant mixtures changes are not significant.

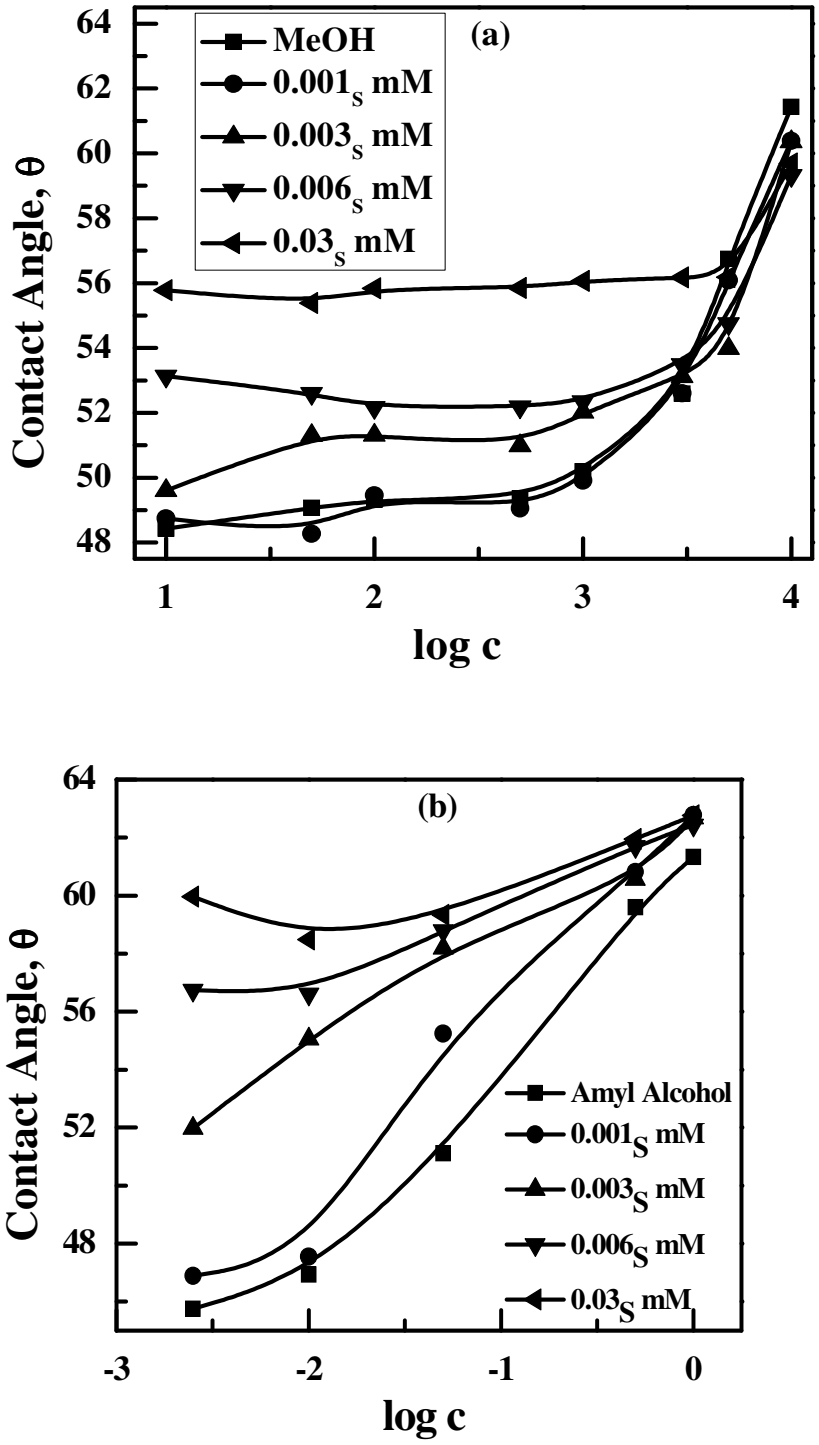


Figure 7.6 Relationship between the values of Concentration (log c) of and change in contact angle of (a) Methanol, (b) Amyl alcohol with varying different Shikakai concentration.

The change in contact angle of Shikakai-amyl alcohol mixtures are slight different than that of methanol-Shikakai mixture, mostly there is a gradual increase in contact angle with the increasing in alcohol concentration.

7.4 Conclusions

The dynamic contact angle study of three different types of plant surfactants, Reetha Shikakai and Acacia and one synthetic surfactant, Triton X 100 on the glass surface revealed that, the wettability of Reetha and Shikakai are more comparing to Acacia. Though there existing straight linear relationship between adhesional tension and surface tension of aqueous surfactant solution, the slop of 0.889 indicates unequal amount of surfactant adsorbed at solid-water interface as well as air-water interface. Whereas no linear relationship between cos θ and inverse of surface tension. There was a linear increase in surface free energy results with increase in concentration as more surfactant molecules were adsorbing at the interface enhancing an increase in contact angle. The change in contact angle of Shikakai-amyl alcohol mixtures are slight different than that of Shikakai–methanol mixture, mostly there is a gradual increase in contact angle with the increasing in alcohol concentration.

Chapter 8

Solution and Wetting Behavior of the Mixed Surfactant System Acacia concinna /Didodecyldimethylammonium bromide.

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8.1 Introduction

More than past two decades there have been increasing trend on mixed surfactant systems based studies compared to that of single surfactants because of their better performance (Zhou and Zhu, 2004; Miller et al., 2004; Zhao et al., 2005; Mohamed and Mahfoodh, 2006; Bergstrom and Bramer, 2008; Rao and Paria, 2009), lower consumption (Wang et al., 2005). Reported studies on mixed surfactant systems are broadly classified into three categories, (i) theoretical aspects to predict different properties (Shiloach and Blankschtein, 1998; Rodenas et al., 1999; Bergstrom and Eriksson, 2000; Bergstrom, 2001, Goldsipe and Blankschtein, 2005), (ii) experimental studies to support the theoretical predictions (Bergstrom et al., 2003; Miller et al., 2004; Bergstrom and Bramer, 2008), (iii) applications to show their performance (Zhou and Zhu, 2004; Zhao et al., 2005; Mohamed and Mahfoodh, 2006; Rao and Paria, 2009). The primary objective of mixed surfactant systems studies is to find out suitable combination of surfactants with synergistic interaction between the head or tail groups. Most of the mixed systems studied are mixture of ionic-nonionic combination but less on two similar ionic or two oppositely charged ionic surfactants. Furthermore, it has been also found that mixed surfactant studies are majority on synthetic-synthetic but rare on natural-synthetic (Konig, et al., 1993; Majhi et el. 1999).

Natural surfactants are a class of surfactants obtained directly from a plant, animal, or microorganism source without any further chemical treatment. In recent years there has been a growing trend of using bio-based or renewable resources for several applications to reduce environmental problem. In case of surfactant formulation, apart from good wetting and surface activity; biodegradability and low ecotoxicity are also extremely important requirement from the environmental viewpoint. Since available literature show there has been less focus on natural surfactants compared to that of synthetic surfactants, practically also they are even not able to substitute a small fraction of worldwide consumption of total synthetic surfactants.

The solution behavior of different synthetic mixed surfactant systems for hydrophobic surface wetting applications are mixtures of similar cationics (Szymczyk et al., 2006), anionics

(Zdziennicka et al., 2003) and nonionics (Szymczyk and Janczuk, 2007), and dissimilar mixtures of both cationic-nonionic (Szymczyk and Janczuk, 2006; Bogdanova et al., 2003; Ghosh Chaudhuri et al., 2012). Apart from the surfactant mixture, an effect of different additives such as electrolytes in mixture of surfactants (Ghosh Chaudhuri et al., 2012) has also been studied thoroughly.

In the industrial process, the use of huge amount of synthetic surfactants which are mostly non-biodegradable, create environmental problem when thrown to the environment. Hence scientists are trying to find the biodegradable or environmentally friendly surfactants for several applications. It has been found that very few on single bio-surfactants (Ozdemira and Malayoglu, 2004; Ishigami et al., 1993) but none on only plant or plant-synthetic mixed surfactant systems. The natural surfactants of plant source may be an alternate option in future because of their easy availability.

This study focuses on the solution behaviour of mixture of a plant-based surfactant Shikakai and a double-chain cationic surfactant DDAB and comparison of wetting behaviour of mixed surfactant systems with the individual single surfactants on PTFE surface. This study shows addition of double-chain cationic surfactant can dramatically enhance the performance of plant-based surfactant, on the other hand mixed system can reduce the consumption of both the surfactants significantly which is desired for any commercial product. The novelty of this work is similar combination mixed surfactant system has not been reported before and also the study has some practical importance.

8.2 Material and Methods

8.2.1 Materials

The structure of cationic double chain Didodecyldimethylammonium (DDAB) bromide and Shikakai are shown in section 4.2.1 and 6.2.1.

8.2.2 Methods

8.2.2.1 Measurement of Surface Tension and CMC

The surface tension and CMC of the surfactants were measured according to the method described in section 3.2.2.1.

8.2.2.2 Measurement of Contact Angle

The contact angle of the surfactant solutions on PTFE surface were measured according to the method described in section 4.2.2.3

8.2.2.3 ^{1}H NMR Measurements

The ^{1}H NMR spectra were recorded with a Bruker Advance 400 Spectrometer (with a ^{1}H proton resonance frequency of 400 MHz) at 25 ºC. D_2O (Aldrich, 99.9%) was used to prepare the surfactant solutions. About 1 ml of each solution was transferred to a 5 mm NMR tube for measurements and chemical shifts (δ) were recorded on the ppm scale. The peaks were referenced with respect to DOH (δ=4.79 ppm) in D_2O.

8.3 Results and Discussion

8.3.1 Solution Behavior of Mixed Surfactant Solutions

The solution behavior of Shikakai and DDAB mixed surfactant solutions was studied using following molar mixing ratios: 98:02, 95:05, 90:10, 80:20, and 50:50 plotted in Figure 8.1. Figure 8.1 depicts that there is a gradual decrease in surface tension to a minimum value of 38.79 mN/m at 0.5 mM Shikakai concentration with a change in slope -11.76, and above that there is no significant change in surface tension. In contrast, DDAB shows two transitions points in the surface tension plot. Initially there is a sharp decrease in surface tension with a slope change at 0.05 mM, further at 0.8 mM a second slope change is observed, for CMC and CVC (critical vesicle concentration) respectively. For DDAB solutions the surface tension values at CMC and CVC are 28.5 and 24.30 mN/m respectively, and beyond CVC the value of surface tension remains almost constant. Shikakai shows higher surface tension value (38.79 mN/m) in contrast to other conventional single-chain cationic (CTAB = 32.99 mN/m), anionic (SDBS = 34.22 mN/m), and nonionic (TX-100 = 31.01 mN/m, Igepal CO-630 = 31.02 mN/m) surfactants (Biswal and Paria, 2011, 2012). Comparison of surface tension results between Shikakai and DDAB shows Shikakai is having higher CMC values as well as higher minimum surface tension at CMC than that of DDAB, which indicates former is lesser surface active. Although the final concentration for minimum surface tension at CVC is little higher for DDAB than Shikakai, but the minimum surface tension is significantly lower (~14.49 mN/m). The solution behavior of Shikakai and DDAB mixed surfactant solutions were studied using different molar mixing ratios mentioned before. The Figure shows at first mixing ratio (2% of DDAB) the CMC of mixed

solution (0.35 mM) is lower than pure Shikakai (0.5 mM) with minimum surface tension value 34.46 mN/m at CMC and a single break point with a change in slope of -13.75 below the CMC. However, when DDAB concentration increases to the ratio of 95:05, the CMC value suddenly decreases to 0.089 mM; subsequently above that mixing ratio, along with CMC the surface tension values at CMC also gradually decreases and become close to that of pure DDAB at 50:50 mixing ratio (as shown in Table 8.1). It is also noteworthy to mention that, in the presence of 5% or above DDAB concentration there are two break points in the surface tension vs. concentration plot similar to that of pure DDAB, the change in break points and surface tension values are presented in Table 8.1. The results indicate as DDAB composition is above 5 mole % DDAB dominates in the mixed micellization process.

Table 8.1 Surface tension values at CMC and CVC.

α_1	γ_{CMC} (mN/m)	Γ_{LG} (mol/m^2 x 10^6)	A_{min} (Å^2)	γ_{CVC} (mN/m)
1	37.94	2.06	80.55	-
0.98	33.40	1.21	137.73	-
0.95	35.64	1.48	112.55	31.59
0.9	34.20	1.39	119.53	30.59
0.8	32.68	1.59	104.17	30.09
0.5	29.51	1.82	90.78	26.22
0	28.04	1.82	91.20	24.31

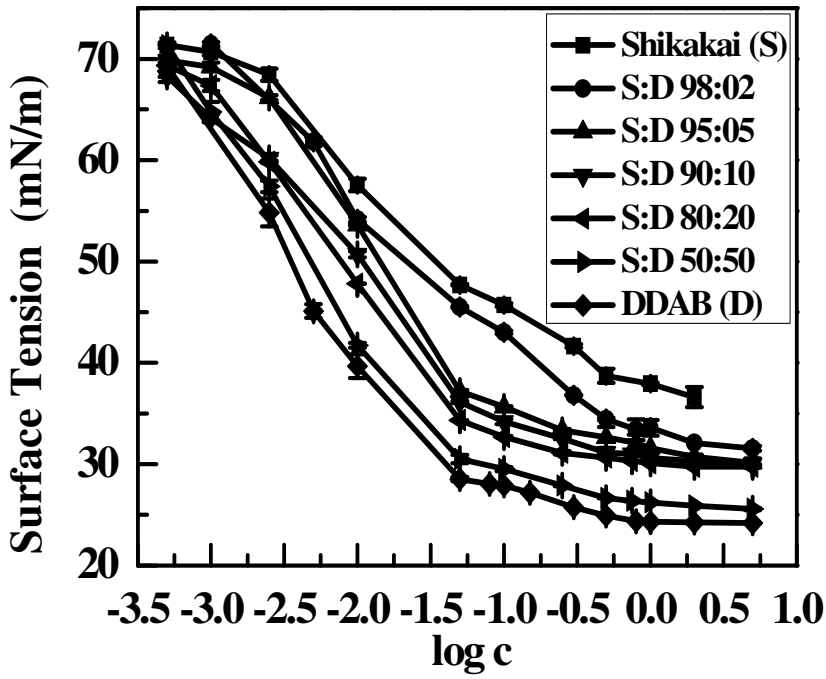

Figure 8.1 The change in surface tension (mN/m) with the concentration (log c) of different surfactants.

When two different (similar or dissimilar types) surfactants are mixed together the mixed solutions behave either ideally or nonideally. In general, nonideal behaviour with synergism has a great technical and academic interest and useful for several applications. To know the actual solution behaviour mixed CMC values was calculated using ideal solution theory (Rubingh, 1979) from equation (8.1) and compared with the experimental values.

$$\frac{1}{CMC_{12}} = \frac{\alpha_1}{CMC_1} + \frac{(1-\alpha_1)}{CMC_2} \qquad (8.1)$$

Where CMC_{12}, CMC_1, CMC_2, are the critical micelle concentrations of binary mixture, Shikakai, and DDAB respectively; and α_1, is the mole fraction of Shikakai in the binary mixture.

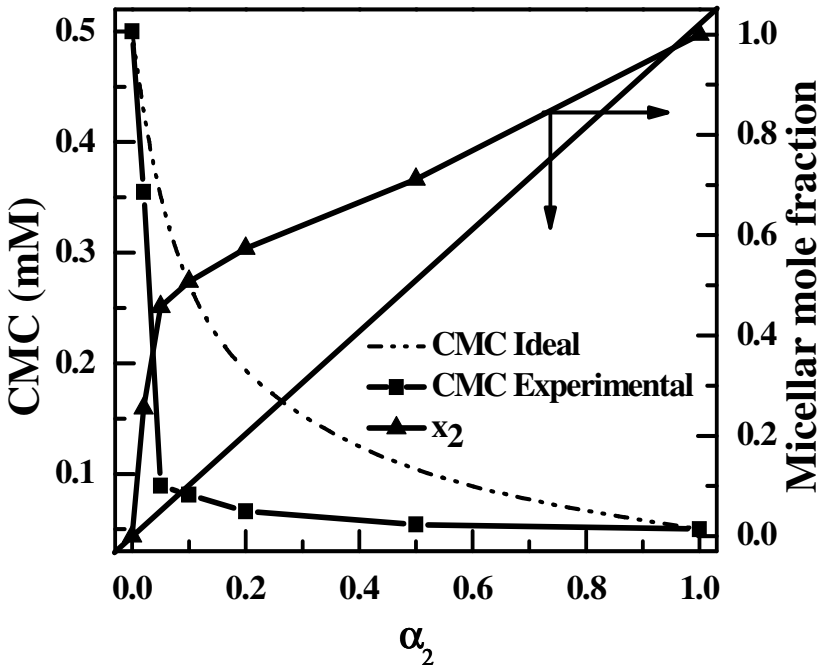

Figure 8.2 Mixture CMC as a function of DDAB composition, for aqueous Shikakai – DDAB, solid line for experimental CMC, dashed line for ideal mixed model, and the solid line with triangle is the micellar mole fraction (x_1) of DDAB.

The experimental and calculated CMC values at different mixing ratios are plotted in Figure 8.2. Interestingly, Figure 8.2 shows there is a huge difference between the experimental and calculated results, although there is a gradual lowering of experimental CMCs with the increasing mole fraction of DDAB and almost no change of that above 0.5 mole fraction of DDAB (α_2). The experimental CMC values are lower than the calculated one using ideal solution theory indicate synergistic interaction between two surfactant molecules with negative deviation. To quantify the nonideal behaviour of binary surfactant mixture, Rubingh's equation (Equation 8.2) of regular solution theory was used to calculate the micellar mole fraction of Shikakai (x_1) by solving iteratively (Rubingh, 1979).

$$\frac{(x_1)\ln(\alpha_1 C_{12} / x_1 C_1)}{(1-x_1)\ln[(1-\alpha_1)C_{12}/(1-x_1)C_2]} = 1 \qquad (8.2)$$

The interaction parameter (β) can be now be calculated by substituting the value of x_1 in equation (8.3).

$$\beta = \frac{\ln(\alpha_1 C_{12} / x_1 C_1)}{(1-x_1)^2} \qquad (8.3)$$

When the value of β is negative synergism in mixed micelle formation, a positive value indicates antagonism, and zero for ideal mixed micelle formation.

The larger the absolute value of β, stronger the nonideality. The calculated values of β at different mixing ratios are reported in Table 8.2. From the Table it can be seen that all the mixing ratios have a synergistic behavior; however, that again varies on the composition. The maximum synergistic behavior was found for 95:05 mixing ratio. This strong synergistic behavior can be attributed to the fact of (i) Vander Waals interaction between the tails of DDAB and hydrophobic part of Shikakai, (ii) strong electrical interaction between positively charged head group of DDAB and carboxyl group of Shikakai. As there is a strong interaction between the surfactant molecules micellization occurs at very low concentration in comparison to pure Shikakai. The CMC of pure Shikakai is higher than DDAB, as a result Shikakai molecules are preferably present in bulk solution than mixed micelle and vice versa for DDAB; additionally the presence of Shikakai reduce the electrostatic repulsive force between the head group of DDAB molecules inside the micelle, that also helps mixed micelle formation at lower concentration. The calculated micellar mole fraction using equation (8.2) are plotted in Figure 8.2, which shows there is a sharp increase in micellar mole fraction DDAB (x_2) with the increase in mole fraction of DDAB (α_2) in bulk. Long distance of separation between the diagonal line and the micellar mole fraction plot also indicate that the mixed solutions nonideal nature.

Table 8.2 Values of micellar mole fraction and interaction parameter β for different mixing ratios.

α_1	CMC_{12}	CMC_{Exp}	x_1	β
1	0.5	0.5	1.000	-
0.98	0.423	0.354	0.744	-1.056
0.95	0.344	0.089	0.542	-5.561
0.9	0.263	0.081	0.492	-4.769
0.8	0.178	0.066	0.427	-4.256
0.5	0.090	0.054	0.288	-3.305
0	0.05	0.05	0	-

8.3.2 Thermodynamic Parameters for the Micellization of Surfactants Mixtures

It is evident from the previous section that there is a favorable interaction between the surfactant molecules during the mixed micelle formation. Now the determination of thermodynamic parameters of the micellization such as free energy (ΔG_{mix}), enthalpy (ΔH_{mix}), and entropy (ΔS_{mix}) play an imporatnt role to get an idea about the spontaneity of the process. The thermodynamic parameters are calculated using the following equations (Rodenas et al., 2003; Ruiz and Aguiar, 2003)

$$\Delta G_{mix} = RT[x_1 \ln(x_1 f_1) + x_2 \ln(x_2 f_2)] \quad (8.4)$$

$$= RT[x_1 \ln(x_1 f_1) + (1 - x_1) \ln\{(1 - x_1)(1 - f_1)\}] \quad (8.5)$$

$$\Delta H_{mix} = RT[x_1 \ln f_1 + x_2 \ln f_2] \quad (8.6)$$

$$\Delta S_{mix} = \left(\frac{\Delta H_{mix} - \Delta G_{mix}}{T} \right) \quad (8.7)$$

Where ΔG_{mix}, ΔH_{mix}, ΔS_{mix} are the free energy (kJ mol^{-1}), enthalpy (kJ mol^{-1}), and entropy (JK^{-1} mol^{-1}) of mixed micellization; f_1 and f_2 are the activity coefficients, x_1 and x_2 are the micellar mole fraction of Shikakai and DDAB respectively. The calculated values at 298 K are presented in Table 8.3.

Table 8.3 Free energy, enthalpy and entropy of mixed micellization.

α_1	x_1	f_1	ΔG_{mix} (kJ mol^{-1})	ΔH_{mix} (kJ mol^{-1})	ΔS_{mix} (JK^{-1} mol^{-1})
0.98	0.744	0.933	-1.903	-0.497	4.718
0.95	0.542	0.312	-5.126	-3.418	5.730
0.9	0.492	0.296	-4.631	-2.914	5.759
0.8	0.427	0.247	-4.268	-2.578	5.671
0.5	0.288	0.187	-3.168	-1.680	4.993

It can be seen from the Table that all the mixtures are having negative free energy of micellization, indicating the mixed micellization process is favourable. It is also important to

note that at 95:05 (Shikakai:DDAB) mixing ratio free energy is more negative which is also consistent with more negative β value. The free energy of mixed micellization is more negative than pure Shikakai but less than pure DDAB. The negative values of enthalpy also indicate the process is exothermic.

8.3.3 ^{1}H-NMR Measurements of Mixed Surfactant Solution

As mentioned in the previous section that the nonideality of the mixed solutions arises mainly may be because of the electrostatic interaction between the Shikakai and DDAB, ^{1}H-NMR was done for single and mixed surfactant solutions to support the hypothesis. ^{1}H NMR spectra of pure DDAB, and their mixture at 95:05 molar ratio in D_2O is represented in (a), (b), and (c) parts of Figure 8.3 respectively. The various protons attached to carbon atoms are labelled on the structure of DDAB and the chemical shift; δ (ppm) values are presented in Table 8.4. The ^{1}H NMR peaks of the protons attached to different carbon atoms of DDAB are marked from letter A to F and their corresponding δ values are identified. A triplet for carbon A (δ_{CH_3}) in the range of 0.836-0.869 ppm are because of three protons of A carbon, B ($\delta_{(CH_2)_7}$) = 1.245, C (δ_{CH_2}) = 1.618, D ($\delta_{(CH_3)_2}$) = 2.503, and a multiplet for E (δ_{CH_2}) in the range of 3.191-3.232 ppm are because of four protons of both the chains, and the six protons of the two-methyl carbons F (δ_{CH_3-N}) appear at 2.977 ppm respectively. The peaks of mixed surfactant solution (Shikakai:DDAB) using 95:05 molar ratio was then compared to see the chemical shift to that of pure DDAB. The mixed surfactant solution shows upfield shifting (towards right) of all the DDAB peaks and peak D disappears as presented in Table 8.4.

In case of pure DDAB surfactant, because of the presence of positive charge on nitrogen atom decreases the electron density mostly on D, E, F carbons, hence results in less shielding or deshielding. Deshielding caused to have higher chemical shift, moving it to the left (downfield). In case of mixture of surfactants, positive charge density on nitrogen atom decreases after interaction with the carboxyl group of Shikakai, as a result magnitude of the deshielding effect decreases, additionally the effect is more as the distance between the charge atom and the proton increases. The NMR results show peak positions shift towards lower δ (upfield) and disappearance of peak D. So the results directly support the interaction between two surfactant molecules.

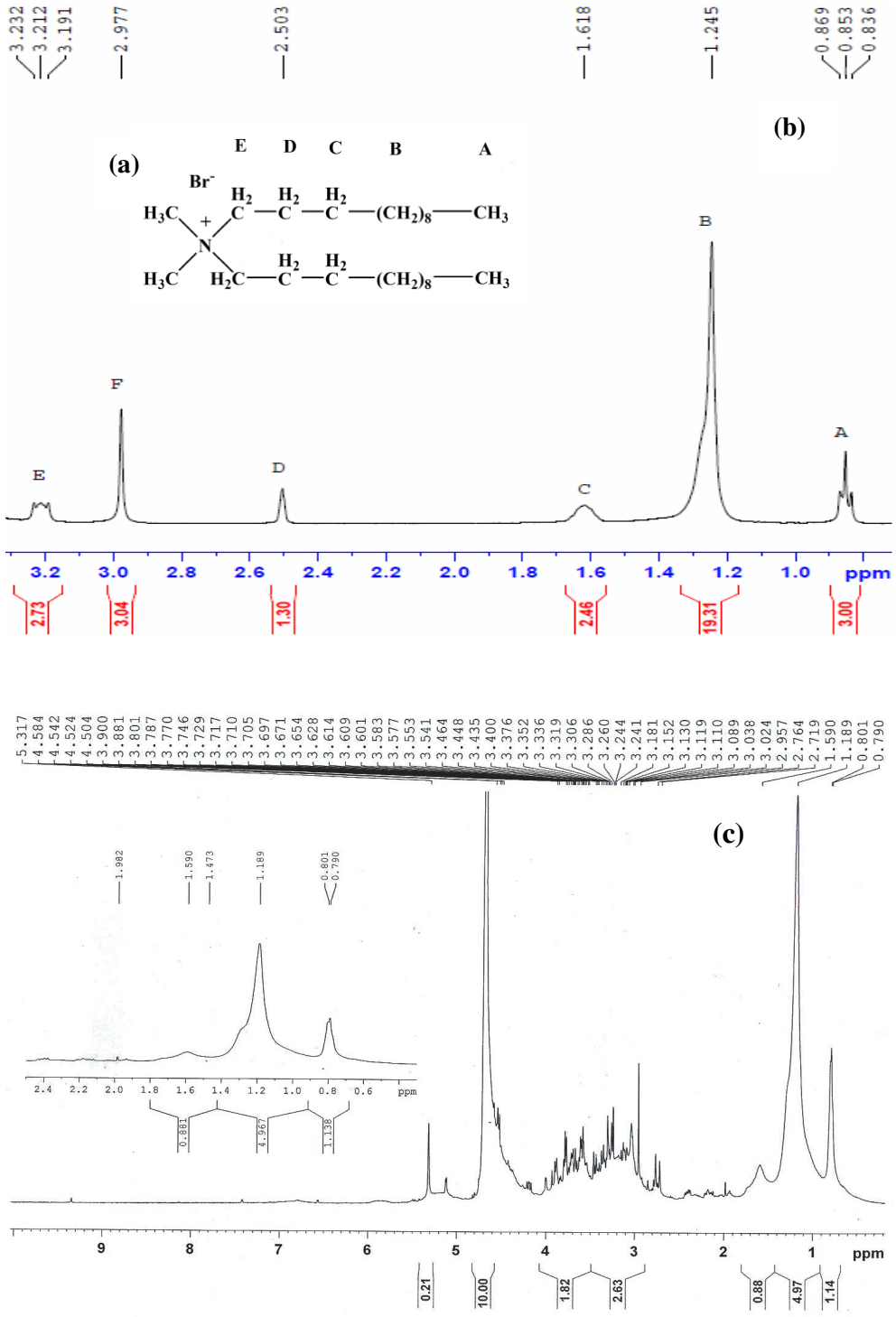

Figure 8.3(a) Labelled structure of DDAB, (b) ^{1}H NMR spectrum of DDAB. (c) ^{1}H NMR spectrum of Shikakai –DDAB mixture at 95: 05 ratio.

Table 8.4 Change in peak position of ^{1}H-NMR spectra measured for pure DDAB, Shikakai and their mixture.

Peak	δ (ppm)$_{DDAB}$	δ (ppm)$_{Mixture}$
A= CH_3	0.836	0.709
	0.853	0.801
	0.869	
B= $(CH_2)_7$	1.245	1.189
C=CH_2	1.618	1.590
D= $(CH_2)_2$	2.503	Disappear
E= (CH_2)	3.191	3.024
	3.212	3.038
	3.232	3.089
F= (N-CH_3)	2.977	2.957

8.3.4 Wettability of Surfactant Mixtures on PTFE Surface

As mixed surfactant solutions show reduction in CMC and surface tension compare to that of pure Shikakai, the mixed solutions were used to test the wettability of a PTFE surface. The contact angle of aqueous solutions using Shikakai, DDAB, and their mixtures of different mixing ratios are presented in Figure 8.4. Pure water shows contact angle value of 116.5° on PTFE surface. With the increasing concentration of pure Shikakai, contact angle (θ) gradually decreases and finally reaches to a plateau value of 98.13º at 0.5 mM concentration with a change in slope of -6.30 and above that it remains almost constant. Whereas in case of DDAB, the contact angle value decreases up to 79°.

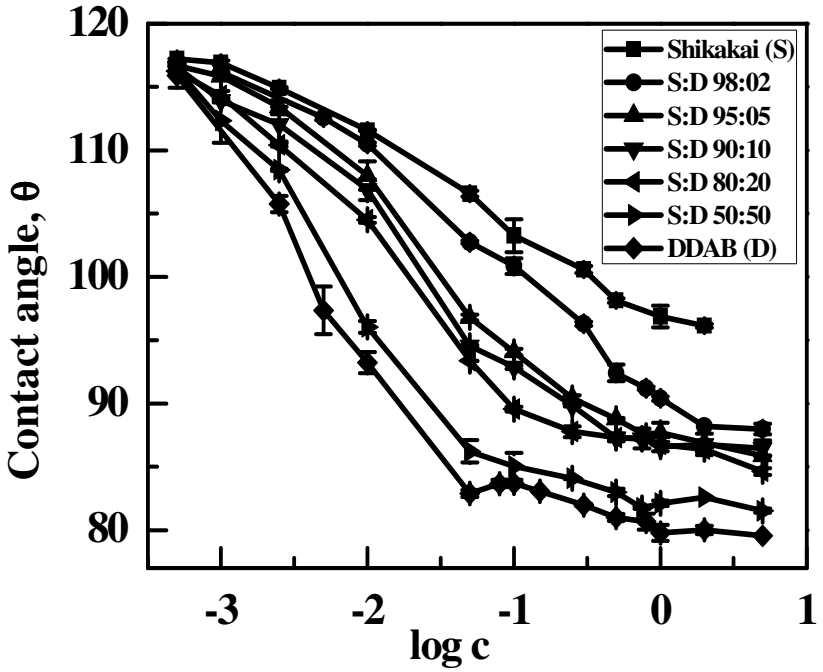

Figure 8.4 The change in contact angle (θ) with the concentration (log c) of different surfactants. The contact angle in the presence of DDAB surfactant is 83° at CMC with first slope -16.85 and above that concentration at CVC the value reduces to 79° with second slope -3.30. So the total decrease in contact angle in the presence of DDAB is more than double (~37°) than that of Shikakai (~ 18°) with respect to pure water.

The wettability of Shikakai and DDAB mixed surfactant solutions on PTFE surface were studied using different molar mixing ratios such as: 98:02, 95:05, 90:10, 80:20, and 50:50. In case of binary mixture, with the increasing DDAB concentration, similar to surface tension plot, contact angle at CMC also decreases gradually for all different mixing ratios. Addition of 2% DDAB to Shikakai, the contact angle value decreases to 92.4° at CMC with a single break point, which is lower than that of the contact angle value of Shikakai (θ = 98.13°) at CMC. Further increasing DDAB concentrations the contact angle values at CMC decreases gradually and 50:50 molar ratio the contact angle at CMC is close to that of pure DDAB. Similar to surface tension plot, when the concentration of DDAB is 5% or above the change because of CVC is prominent, the contact angle values at CMC and CVC for different mixing ratios are presented in Table 8.5.

A comparative analysis of contact angle change and surfactant consumption in terms of mole % of different synthetic and Shikakai-DDAB mixed surfactants with respect to Shikakai is presented in Table 8.6. The negative values of Δθ and mole % consumption indicates lower

Table 8.5 The contact angle (θ) values at CMC and CVC for different mixing ratios.

α_1	θ_{CMC}	θ_{CVC}
1	98.13	_
0.98	91.19	_
0.95	90.43	87.69
0.9	92.86	87.19
0.8	89.54	86.75
0.5	86.21	81.75
0	83.67	79.78

Table 8.6 A comparison of minimum contact angle and surfactant consumption in mole % with respect of Shikakai for different single and mixed surfactant systems.

Surfactant		θ^{o}_{min}	Conc. (mM)	Δθ	Consumption in mole %
Shikakai		98.13	0.5		
DDAB	CMC	83.67	0.05	-14.46	-90
	CVC	79.78	0.8	-18.35	+60
TX-100		80.42	0.15	-17.71	-70
Igepal CO 630		82.79	0.08	-15.34	-84
CTAB		84.06	0.9	-14.07	+80
SDBS		86.76	1.5	-11.37	+200
Shikakai: DDAB	98:2	91.19	0.35	-6.94	-29.
	95:5	87.69	0.870	-10.44	+74.19
	90:10	87.19	0.841	-10.94	+68.27
	80:20	86.75	0.822	-11.38	+64.44
	50:50	81.75	0.812	-16.38	+62.56

contact angle and consumption than that of Shikakai. Highest contact angle of Shikakai indicate inferior interfacial property, however addition of DDAB enhance the wetting property as well as reduce the consumption of surfactant. The Table clearly shows that at 98:2 mixing ration contact

angle is ~ 7º lower than pure Shikakai and consumption is 29% lower than pure Shikakai; however when the mixing ratio is 50:50 contact angle is 16.3 º lower but consumption increases to 62.5%.

8.3.5 Adsorption of Surfactants at PTFE–Water and Air–Water Interfaces

The change in contact angle in the presence of aqueous surfactant solutions is closely related to the adsorption density as well as the adsorption pattern on the solid surface. The contact angle measurements indirectly gives some idea about the surface excess at solid-liquid interface compared to that of air-water interface; which can be obtained again from the surface tension results. It has been found before that the surface excess values at PTFE-water interface are less than that of air-water for the pure surfactants, but exact % reduction depends on type of surfactants (Biswal and Paria, 2011; Ghosh Chaudhuri and Paria, 2009).

In the case surfactant mixture also the plot of adhesion tension ($\gamma_{LG} \cos \theta$) vs surface tension shows linear relationship and shown in Figure 8.5. The slopes of linear fit using equation (8.8) for pure and surfactant mixture of different mixing ratios are tabulated in Table 8.7.

$$\gamma_{LG} \cos \theta = a\, \gamma_{LG} + b \qquad (8.8)$$

where a and b are slope and intercept for the linear fit respectively.

The Table 8.7 shows pure Shikakai, DDAB, and their mixture of different rations have slope less than 1. This indicates that the surface excess of surfactant at PTFE – water interface is lower than that of air –water interface. It can be seen from the Table that the slope value is higher than the pure surfactants till 80:20 mixture, when the ratio is 50:50 the slope is close to that of pure DDAB. The increasing adsorption density at PTFE-water interface than that of air-water is may be because of (i) strong interaction between the surfactant molecules in the bulk solutions for those mixing ratios, (ii) reduction in repulsive fore between the head groups of DDAB in the presence of Shikakai.

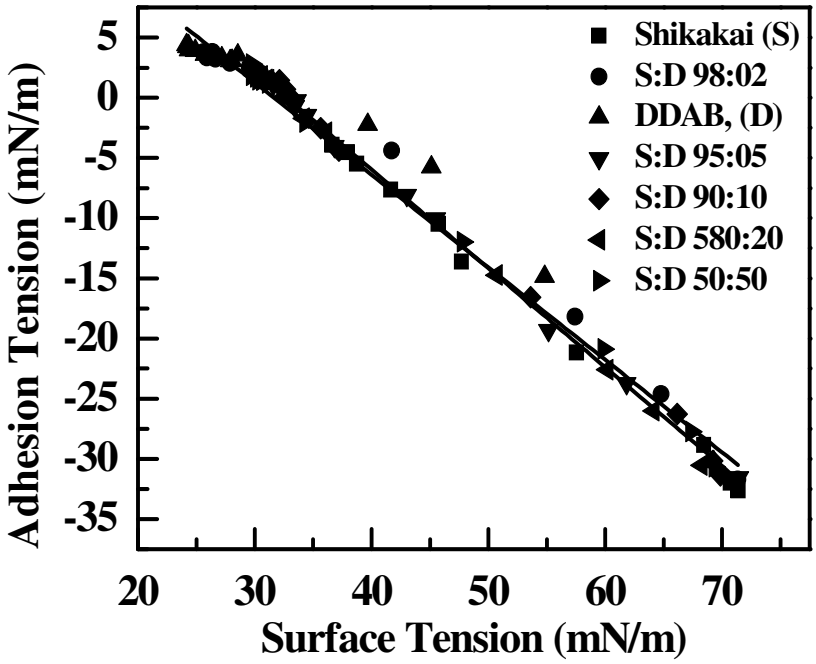

Figure 8.5 The change in adhesional tension (γ_{LG} cos θ) versus surface tension (γ_{LG}) of different surfactants.

Table 8.7 Values of 'a' and 'b' for from the adhesional tension and surface tension plot for different mixing ratios.

α_1	a	b	R^2
1	-0.782	24.99	0.999
0.98	-0.823	27.038	0.998
0.95	-0.826	27.264	0.997
0.9	-0.834	27.227	0.999
0.8	-0.802	26.081	0.998
0.5	-0.752	23.977	0.989
0	-0.745	23.587	0.971

8.3.6 Work of Adhesion

The work of adhesion, W_A, of a liquid on the solid are determined using equation (4.10) and (4.11). Taking into account equation (4.11), the measured values of the contact angles for aqueous solutions of surfactants on PTFE surfaces, and the data of their surface tension, the

values of the work of adhesion of solutions to the PTFE surfaces was calculated, and are presented in Figure 8.6.

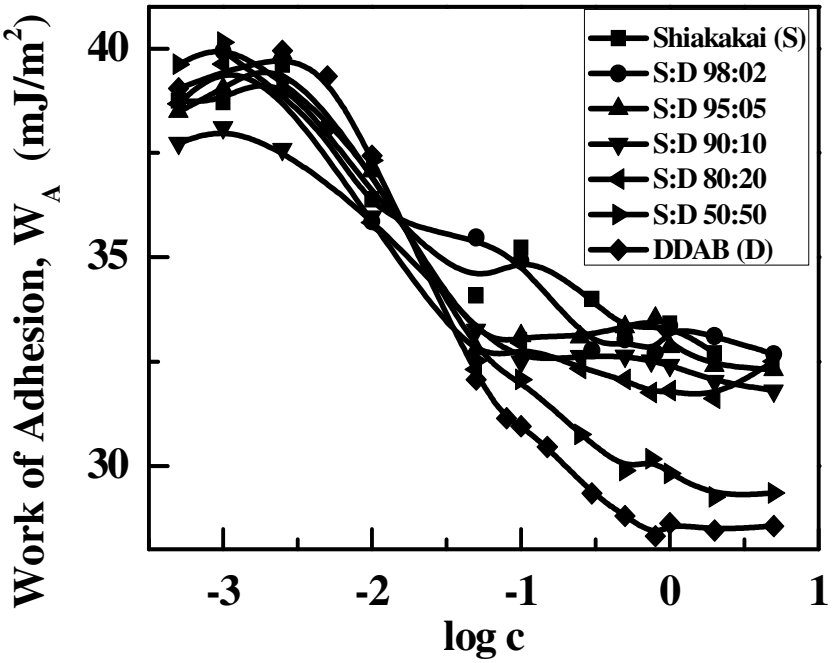

Figure 8.6 The change in work of adhesion (W_A) with the concentration (log c) of different surfactants.

The works of adhesion of pure Shikakai and DDAB surfactant solutions on PTFE surfaces above the CMC are 32.69 and 28.55 mJ/m^2 respectively which are very less compare to the work of adhesion of pure water for PTFE surfaces which is 39.59 mJ/m^2. Though, the final work of adhesion value at CMC, for individual surfactants and their mixtures decreases with the increase in mole fraction of DDAB, still for all those mixing ratios, the values lie in between these two pure ones.

8.4 Conclusions

The mixture of Shikakai and DDAB show strong synergistic interaction between the head group of DDAB and carboxyl group of Shikakai confirmed by ^{1}H NMR. The synergistic behavior in terms of interaction parameter (β = -1.056 to -5.561) using regular solution theory was calculated and found to be negative for entire mixing ratios with maximum non-ideality (β = -5.561) at 95:05 ratio.

Pure DDAB forms vesicle in the solution, however in the mixed solutions when the concentration of DDAB is 5 mol % or above vesicles are formed. Pure Shikakai and DDAB solutions show minimum contact angle values of 98.13 and 79.78° on PTFE surface. In case of surfactants mixture, addition of 2 mol % DDAB on Shikakai show ~ 7º lower contact angle than pure Shikakai and the consumption is 29% lower than pure Shikakai; however 50% DDAB is added contact angle is 16.3 º lower but consumption increases to 62.5%.

Chapter 9

Conclusions and Suggestions for Future work

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9.1 Conclusions

Overall conclusions of the thesis according to the organization of the chapters are arranged as follows:

Adsorption of different types of synthetic surfactant and natural plant surfactant at air–water interface and solid–water interface and its effect on wettability effect on PFTE and glass surfaces are investigated here. In order to enhance the wettability of pure single surfactants additives like alcohol and surfactant mixtures also studied.

The rate of adsorption of three synthetic surfactants TX–100, SDBS, and CPB on PTFE surface is very fast; within 10 minutes the equilibrium is reached. Pseudo–second–order kinetic model fits well for the adsorption kinetics of all three surfactants with the following order of rate constant values with a minimum difference: CPB > TX–100 > SDBS. The adsorption isotherms of TX–100 show Langmuir type but SDBS and CPB are better fit with Freundlich type model. In the presence of electrolytes, isotherms of both the ionic surfactants show better fitting with Langmuir type isotherm. When the initial concentration of the ionic surfactant is constant and far below the CMC, the addition of electrolytes show there is a linear relationship between the amount of surfactant adsorbed and ionic strength of the electrolyte solutions. The increasing order of the slopes in the linear portion for SDBS is: Na_2SO_4 < NaCl << $CaCl_2$ and that for CPB: NaCl < $CaCl_2$ << Na_2SO_4. The area occupied per molecule (A_m) also changes linearly with the Debye length in the presence of electrolytes for both the ionic surfactants. The A_m is mainly dependent on Debye length but independent on the types of electrolytes when mono–valance counter ion is present. Whereas, in the presence bi–valance counter ion for a particular Debye length the difference in A_m is observed. The difference in A_m in the presence of mono– and bi–valance counter ion is more at higher Debye length. The main mechanism of increase in amount adsorbed for both the surfactants can be attributed to the decrease in the electrostatic repulsion between the surfactant headgroups, as a result, closer packing of the surfactant molecules at the surface. This study gives an idea about the adsorption behavior of anionic and cationic surfactants on a hydrophobic surface in the presence of electrolytes. The study may be useful in

some applications like wetting, colloid stability, dispersion of polymers etc. where surfactant adsorption is an important parameter; moreover, surfactant consumption can also be reduced by adding small amount of electrolytes to the surfactant solutions.

The adsorption kinetics and isotherms of TX-100 and Igepal CO-630 were found to follow pseudo-second-order kinetics and the Langmuir isotherm model, with a higher adsorption constant rate constant and a higher Langmuir constant for Igepal CO-630. The decrease in contact angle with increasing surfactant concentration follows a trend similar to that of the adsorption isotherm of the respective surfactant. The free energy of wetting becomes more negative with increasing surfactant concentration, indicating that the process is spontaneous for both surfactants. The Hamaker constant and work of adhesion decrease gradually with increasing surfactant concentration and ultimately reach plateau regions above the CMC. Igepal CO-630 shows a lower work of adhesion and Hamaker constant than TX-100. The change in the polar component of the interaction term with the PTFE-water interfacial tension follows the same linear relationship for both surfactants, so the PTFE-water interfacial tension is independent of the type of surfactant. Igepal CO-630 has a lower CMC value and better wetting properties at low concentration than TX-100, as well as comparable properties near the CMC. As a result, the use of Igepal CO- 630 as a wetting agent might be more beneficial than the use of TX-100 because of lower consumption in the process and possibly higher biodegradability in nature (because of the presence of a straight-chain hydrocarbon tail).

Double-chain cationic (DDAB) and anionic (AOT) surfactants show a lower value of minimum surface tension at the CMC compared to that of commonly used single-chain surfactants. The plot of surface tension vs concentration of DDAB shows two break points in slope because of the formation of micelle first and then vesicle, with higher slope at the micellar region. The surfactant concentration to achieve plateau level surface tension and the minimum surface tension values are lower for DDAB than AOT; subsequently adsorption density of DDAB is higher at the air–water interface than AOT. The wettings of the PTFE surface in the presence of both the double-chain surfactants are similar in terms of a decrease in contact angle and much better than the conventional single-chain surfactants; however, the final concentration required for DDAB is lower than AOT. In the case of the glass surface the increase in contact angle is slightly more for DDAB. There is a linear relationship of adhesion tension and surface tension with slopes of −0.759 and +0.840 on PTFE and glass surfaces, respectively, for both

surfactants; the slope values below one indicate surface excess of surfactant molecules at the solid–water interfaces are less than that of the air–water interface. DDAB solutions show a critical adhesion tension for the PTFE–water and glass– water interfaces, where both the hydrophilic and hydrophobic surfaces are having equal adhesion tension and wettability. The free energies of wetting on the PTFE surface are more negative in the presence of surfactant solutions than pure water. However, on the glass surface the free energies of wetting are less than pure water but free energies of wetting on the glass surface are still more negative than PTFE for both surfactants. Finally, it can be concluded that the double-chain cationic and anionic surfactants are having better wettability on the PTFE surface compared to single-chain surfactants. The use of cationic double-chain surfactant (DDAB) may reduce the consumption of surfactant to a value of 93 and 60%, respectively, compared to that of CTAB and AOT for wetting of the PTFE surface. In the industrial applications where the consumption is huge these findings may have a great importance from the economic and environmental of view points.

The surface tension measurements show surface tensions at CMC for Reetha and Shikakai are very close (~ 38.3 mN/m) but little higher for Acacia (~ 43.6 mN/m), which in turn show surface excess values at air-water interface for Reetha and Shikakai are higher than Acacia. The adsorption kinetics of these surfactants on PTFE surface show adsorption comparatively fast and approximately within ~20 minutes equilibrium reaches. A Langmuir-type isotherm fits well for all three surfactants studied here. The maximum adsorption capacities of three surfactants at PTFE-water interface are found to be in the following order: Shikakai > Reetha ≈ Acacia. The comparisons of area per molecule at air-water and PTFE-water interfaces show that at PTFE-water interface adsorption densities of Reetha, Acacia, and Shikakai are 0.628, 0.734, 0.866 times less respectively than that of air-water interface. The change in contact angle on PTFE surface by the surfactant solutions also follow similar trend to that of adsorption density; for Reetha, Acacia, and Shikakai are 109.88°, 109.02° and 98.13° respectively. The contact angle studies also independently support lower adsorption density at PTFE-water interface than air-water interface for all three surfactants. These findings may be useful for application of these surfactants for general wetting processes, detergency, shampoo and other applications. More importantly they can also be treated as environmentally green.

The addition of methanol and amyl alcohol to the Shikakai solution show there is synergistic interaction between the alcohol and Shikakai molecules and that is more for amyl

alcohol. Since the interaction is more for amyl alcohol consumption of alcohol is also 1000 times lower than methanol to get similar surface tension reduction. When the concentration of Shikakai is constant with the increasing concentration of alcohols up to a certain concentration of alcohol reductions in surface tension and contact angle are more than that of pure solutions of similar concentrations because of synergistic interaction.

The wetting study of three different types of plant surfactants, Reetha Shikakai and Acacia and one synthetic surfactant, Triton X 100 on the glass surface revealed that, the wettability of Reetha and Shikakai are more comparing to Acacia. Though there existing straight linear relationship between adhesional tension and surface tension of aqueous surfactant solution, the slop of 0.889 indicates unequal amount of surfactant adsorbed at solid-water interface as well as air-water interface. Whereas no linear relationship between cos θ and inverse of surface tension. There was a linear increase in surface free energy results with increase in concentration as more surfactant molecules were adsorbing at the interface enhancing an increase in contact angle. The change in contact angle of Shikakai-amyl alcohol mixtures are slight different than that of Shikakai–methanol mixture, mostly there is a gradual increase in contact angle with the increasing in alcohol concentration.

The mixture of Shikakai and DDAB show strong synergistic interaction between the head group of DDAB and carboxyl group of Shikakai confirmed by ^{1}H NMR. The synergistic behavior in terms of interaction parameter (β = -1.056 to -5.561) using regular solution theory was calculated and found to be negative for entire mixing ratios with maximum non-ideality (β = -5.561) at 95:05 ratio.

Pure DDAB forms vesicle in the solution, however in the mixed solutions when the concentration of DDAB is 5 mol % or above vesicles are formed. Pure Shikakai and DDAB solutions show minimum contact angle values of 98.13 and 79.78° on PTFE surface. In case of surfactants mixture, addition of 2 mol % DDAB on Shikakai show ~ 7º lower contact angle than pure Shikakai and the consumption is 29% lower than pure Shikakai; however 50% DDAB is added contact angle is 16.3 ° lower but consumption increases to 62.5%. These findings again can be useful in many industrial and domestic cleaning processes.

9.2 Suggestions for Future Work

Following suggestions are made for the future work.

1. Solution and adsorption behavior of Shikakai-anionic and Shikakai-nonionic surfactants mixture may also be studied to the behavior.
2. Mixed surfactant behavior with other two plant surfactants can also be studied.
3. Effect of electrolytes on mixed surfactant system may also be studied.
4. Adsorption behavior on solid surfaces can be supported by AFM studies.
5. Shikakai-DDAB mixed surfactant system can be used for other applications also.

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List of Publications

1. **Nihar Ranjan Biswal** and Santanu Paria. Comparison of Wetting Behavior of Cationic and Anionic Double Chain Surfactants with That of Single Chain on PTFE and Glass Surfaces. ***Ind. Eng. Chem. Res.*** 2012, 51, 10172−10178.
2. **Nihar Ranjan Biswal** and Santanu Paria. Wetting of TX-100 and Igepal CO-630 Surfactants on a PTFE Surface. ***Ind. Eng. Chem. Res.*** 2011, 50, 6138-6145.
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Effect of Electrolyte Solutions on the Adsorption of Surfactants at PTFE−Water Interface

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Adsorption of ionic and nonionic surfactants on low surface energy hydrophobic PTFE−water interfaces in the absence and presence of electrolytes have been studied here. The objective of this study is to see the surfactant adsorption behavior in the presence of electrolytes that may reduce the consumption of surfactants. The kinetics of adsorption fits well pseudo-second-order kinetic model for the three surfactants studied here. Adsorption isotherms of TX-100 follow Langmuir type, whereas sodium dodecylbenzene sulfonate (SDBS) and cetylpyridinium bromide (CPB) follow Freundlich type. However, in the presence of electrolytes both the ionic surfactants show better fitting with Langmuir type isotherm. The effect of electrolytes on the surfactant concentration far below the CMC shows there is a linear increase in amount adsorbed with the increase in ionic strength of the electrolyte mainly due to reduction in headgroup repulsion and finally reaches a plateau level when the equilibrium concentration reaches CMC at that electrolyte concentration.

1. Introduction

Surfactant adsorption at solid−liquid interfaces has been extensively studied by many researchers for a long period of time because of its versatile applications. The adsorption of surfactants at the interfaces is always there whenever they are used in different applications. Surfactants can change the solid surface property from hydrophilic to hydrophobic and vice versa by adsorption. There are many studies available on the surfactant adsorption at hydrophilic surfaces, compared to only a few at hydrophobic surfaces. Surfactant adsorption at hydrophobic solid−water interfaces has applications such as wetting,[1] stabilization of polymer suspension,[2] surface cleaning,[3] etc. To see the effectiveness of these applications there are also some studies available on contact angle and wetting properties of different hydrophobic polymer surfaces such as polytetrafluoroethylene (PTFE)[4−8] and both PTFE and polymethyl methacrylate (PMMA)[9,10] where surfactant adsorption is inherently involved. In general, hydrophobic or polymer surfaces have low surface energy and are difficult to suspend or wet by aqueous media for different applications. The adsorption of surfactants on hydrophobic surfaces overcomes those difficulties by changing the surface properties. In this regard, apart from the adsorption at solid−liquid interface, surface tension of the aqueous solution which is related to the adsorption at air−liquid interface is equally important. The effect of ionic strength or electrolytes can significantly influence the critical micellar concentration (CMC), surface tension value at CMC, and adsorption densities at air−liquid and solid−liquid interfaces which may have great importance in many applications.

Surfactant adsorption studies on polymer surfaces are mainly reported at PTFE,[11−15] polystyrene,[2,16−19] polyvinyltoluene (PVT),[20] and PMMA[21] surfaces. Dixit and co-workers studied single cationic surfactants[14] and cationic−nonionic mixed surfactants systems on PTFE surface.[13,15] In a single cationic surfactant system they have studied the effects of chain length of alkyltrimethyl ammonium bromide and pyridinium chloride surfactants. The isotherm consisted of two plateau regions due to formation of hemimicelle. In the cationic−nonionic (CTAB-NP_n) mixed surfactant system adsorption of either cationic or nonionic was enhanced below the CMC[13] and adsorption of CTAB decreased with the increase in mole fraction of nonionic surfactants (NP_n) above the CMC due to formation of mixed micelle. Connor and Ottewill[16] showed the formation of hemimicelle for cationic surfactant on polystyrene surface; they suggested that the particles have two types of sites for adsorption: charged sites which interact with the cationic headgroup of the surfactant and adsorbtion through tailgroup on the hydrophobic sites. The adsorption of nonionic nonylphenol polyethylene oxide of different chain lengths on PMMA surface shows Langmuir isotherm due to the formation of monolayer.[21]

Regarding the effect of electrolytes on surfactant adsorption, it is observed that although there is much literature available on hydrophilic surfaces[22−26] there is not any on hydrophobic surfaces. Atkin et al.[23] found the addition of electrolytes shifted the adsorption isotherm of CTAB toward lower concentration with increase in maximal surface excess at silica−water interface and Br^- ion was more effective to increase the surface excess of CTAB than that of Cl^- to the CTAC system. Paria and Yuet[25] concluded the adsorption of cationic surfactant on negatively charged hydrophilic surface (sand) linearly increased with the increasing electrolyte concentration at a constant surfactant concentration below the CMC mainly due to reduction of repulsion between the surfactant headgroups. Also, between the two forces (i) attraction between the solid surface and surfactant headgroups and (ii) repulsion between the headgroups, the latter was predominant for increasing the surface excess in the presence of electrolytes. Howard et al.[26] showed that there exists a common intersection point (CIP) at which a particular surfactant concentration below this point an increase in electrolyte concentration reduced surfactant surface excess, and at concentrations above this point an increase in electrolyte concentration led to an increase in surfactant surface excess.

From the literature it is clear that limited studies are available on the adsorption of surfactants (kinetics and isotherm) at PTFE surface. Although there are some studies available on the effect of electrolytes on surfactant adsorption at the hydrophilic solid−liquid interface, there are no studies on PTFE or other hydrophobic surfaces to the best of our knowledge. In this paper,

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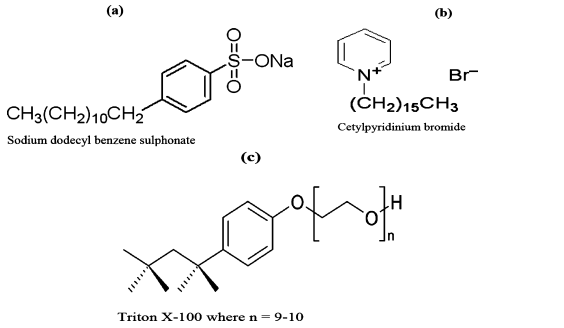

Figure 1. Structures of the surfactant molecules: (a) SDBS, (b) CPB, (c) TX-100.

we have studied the adsorption kinetics and the isotherms of three different surfactants (anionic, SDBS; cationic, CTAB; and nonionic, TX-100; Figure 1) at PTFE surface. In addition, electrolytes effects have also been studied on the adsorption of anionic and cationic surfactants at PTFE−water interface. The objective of this paper is to study the adsorption behavior of surfactants in the presence of electrolytes to reduce the surfactant consumption. Food processing and many other industrial operations use PTFE-coated reactors and pipes; regular cleaning of those is essential, especially in food processing operations. The presence of electrolyte along with the surfactants in the cleaning process may reduce the consumption of surfactant along with the increase in adsorption and wetting properties. In many cases, after the cleaning process surfactants are disposed in the environment; in this situation, less consumption of surfactant may also reduce environmental problems.

2. Materials and Methods

2.1. Materials. Triton X-100 (TX-100; 99% purity) was purchased from Loba Chemicals Pvt. Ltd., India. Cetylpyridinium bromide (CPB, 99%) from Rankem, India and sodium dodecylbenzene sulfonate (SDBS) of technical grade (Cat no. 28 995-7) from Sigma-Aldrich chemicals, Germany were purchased and used without any further purification. The electrolytes NaCl and Na_2SO_4 were purchased from Rankem and $CaCl_2$ was from Merck, India. The PTFE powder used for adsorption experiments was purchased from Pragati Plastics Pvt. Ltd., Delhi, India. Aqueous solutions of individual surfactants were made by ultrapure water (Sartorius, Germany) of 18.2 MΩ·cm resistivity, 71.5 mN/m surface tension, and 6.5−7 pH at 25 ± 0.5 °C. For all the experiments, a single surfactant solution of desired concentration was prepared by diluting a concentrated stock solution.

2.2. Methods. The surface tension of aqueous solutions of surfactants was measured at 25 ± 0.5 °C by the Wilhelmy plate technique with a surface tensiometer (DCAT 11EC, Data physics, Germany). After measurement of each concentration, the platinum plate was cleaned with water followed by acetone and burned in alcohol flame for complete removal of adsorbed surfactant. The particle size of the PTFE powder was measured using a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., U. K.) and found that the average particle size 115.7 μm. The zeta potential of PTFE powder was measured by equilibrating 5 mg of powder in 50 mL of 0.01 M KCl solution using Zetasizer Nano ZS (Malvern, U.K.). The zeta (ζ) potential was calculated from the electrophoretic mobility using Smoluchowski's equation and found to be −4.82 mV. The specific surface area (BET) of the PTFE powder was measured twice by N_2 adsorption−desorption studies at liquid nitrogen temperature (−195.8 °C) using Autosorb-1 (Quantachrome, USA) and the average value was found to be 4.3 $m^2\ g^{-1}$. Prior to the analysis, samples were degassed at 200 °C. Low nitrogen adsorption at relative pressure (P/P_0) values <0.2 indicates the absence of microporosity, which is also reflected in the low value of the BET surface area, 4.3 $m^2\ g^{-1}$.

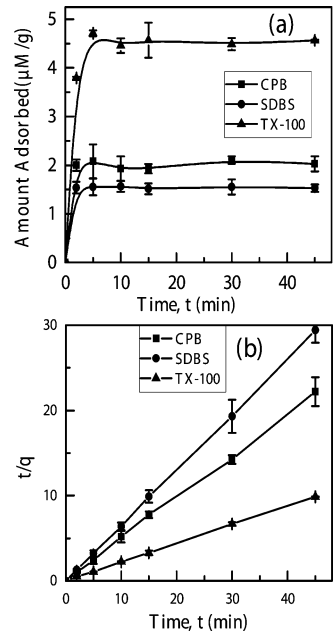

Figure 2. (a) Adsorption kinetics of CPB, SDBS, and TX-100 on PTFE powder using 0.2 mM surfactant concentration. (b) Linear fitting of pseudo-second-order kinetics.

For the adsorption experiments a volume of 10 mL of surfactant solution of different concentrations was taken in 60-mL plastic bottles, and 0.1 g of PTFE powder was used for all the experiments. The adsorption isotherm was constructed using nine different surfactant concentrations (0.05, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1, 2 mM) from below to above CMC. All the measurements were carried out at neutral pH 6.5−7. For the electrolyte effect, the desired concentration of electrolyte was mixed with the surfactant solution before addition of solid. The bottles were shaken well for 2 h at 25 ± 0.5 °C on an incubator shaker. PTFE particles were separated from the mixture by centrifugation at 5000 rpm. The concentrations of the surfactants solutions before and after the adsorption were determined by UV−vis spectrophotometer (Jasco, V-530, Japan) at λ_{max} 223, 224, and 258 nm for TX-100, SDBS, and CPB, respectively, using their respective calibration curves (absorbance vs concentration) constructed from the known concentrations. The experiments were repeated at least thrice and the average data were plotted. The amount of surfactant adsorbed was determined by the following equation

$$\Gamma = \frac{(C_i - C_{eq})V}{1000m} \tag{1}$$

where C_i and C_{eq} are the initial and equilibrium concentrations (mM), V is the volume of surfactant solution (mL), and m is the mass of the adsorbent (g).

3. Results and Discussion

3.1. Adsorption Kinetics. Adsorption kinetics of three different surfactants (CPB, SDBS, and TX-100) at 0.2 mM concentration at PTFE−water interface are presented in Figure 2a. The adsorption kinetics are studied to know the rate as well

Table 1. Pseudo-First-Order and Pseudo-Second-Order Kinetic Parameters for SDBS, CPB, and TX-100

	pseudo-first-order			pseudo-second-order		
surfactant	k_1 (min^{-1})	q_e ($\mu M \cdot g^{-1}$)	R^2	k_2 ($g \cdot (\mu M \cdot min)^{-1}$)	q_e ($\mu M \cdot g^{-1}$)	R^2
CPB	0.035	0.148	0.297	0.976	1.074	0.999
SDBS	0.064	0.084	0.140	0.811	1.102	0.998
TX-100	0.115	0.189	0.617	0.914	1.217	0.999

as equilibrium time for the adsorption process. At very low surfactant concentration the amount of surfactant adsorbed as well as the differences among the surfactants are less, hence the concentration was chosen for kinetics where the difference is more. It is found from the figure that within 10 min all three surfactants reached equilibrium and the rate of adsorption is also very fast. Figure 2a shows that at 0.2 mM concentration the surfactants are following the order of amount adsorbed at equilibrium TX-100 > CPB > SDBS. To know the rate at which adsorption takes place there are generally two commonly used kinetic models, i.e., pseudo-first-order and pseudo-second-order, to identify the nature of surfactant adsorption. The pseudo-first-order kinetics can be presented as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

Equation 2 is then integrated for the conditions $t = 0$ to t and $q = 0$ to q_t and rearranged to get

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

The pseudo-second-order kinetics can be presented as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

The eq 4 is then integrated for the conditions $t = 0$ to t and $q = 0$ to q_t and rearranged to get

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

or

$$\frac{q_t}{t} = \frac{h}{1 + k_2 q_e t} \tag{6}$$

where q_t and q_e are amount of surfactant adsorbed at time t and at equilibrium in $\mu M \cdot g^{-1}$, and k_1 (min^{-1}) and k_2 ($g \cdot \mu M^{-1} \cdot min^{-1}$) are adsorption rate constants for pseudo-first-order and pseudo-second-order, respectively. h ($\mu M \cdot g^{-1} \cdot min^{-1}$) can be regarded as the initial sorption rate as q_t/t, when t approaches 0. Hence,

$$h = k_2 q_e^2 \tag{7}$$

The adsorption rate constants of both the models calculated by eqs 3 and 5 as shown in Table 1. The high values of correlation coefficient (R_2^2) for the fitting obtained from the kinetic plots using the second model suggest that adsorption of surfactants on PTFE surface can be better expressed by the pseudo-second-order model as shown in Figure 2b. The results show the order of initial adsorption rates, TX-100 > SDBS > CPB.

3.2. Adsorption Isotherm. Figure 3 represents the adsorption isotherms of three surfactants on PTFE surface. From the figure it is clear that the shapes of three different isotherms are not similar with different maximum amount adsorbed at saturation. The nature of the adsorption isotherm for TX-100 is apparently different, whereas, the other two ionics are close to similar. At lower surfactant concentration the change in amount adsorbed is not significant, whereas at higher concentration there is a significant change among the three surfactants. The order of equilibrium amount adsorbed at the plateau level is CPB > TX-100 > SDBS.

There are two types of models, Langmuir and Freundlich isotherms, generally used to correlate the amount adsorbed and the equilibrium concentration for the adsorption of surfactant molecules on a solid surface. The Langmuir and Freundlich isotherms may be expressed as the following equations:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{8}$$

$$\log q_e = \log a + \frac{1}{n}\log C_e \tag{9}$$

where q_m is equilibrium amount adsorbed ($\mu M \cdot g^{-1}$), b is the adsorption constant of Langmuir equation (mM^{-1}), C_e is the equilibrium concentration of surfactants in the solution (mM), a is a constant or coefficient of Freundlich isotherm equation representing the adsorption capacity, and n is a constant (reciprocal of the exponent of the Freundlich isotherm equation) depicting the adsorption intensity. When there is a negligible intermolecular interaction between the adsorbed surfactant molecules i.e., only monolayer of adsorbate is formed, the Langmuir model works quite well. In this study we have applied two models to test the better fitting of these isotherms. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients (R^2) are listed in Table 2.

From Table 2, it is clear that TX-100 is following Langmuir isotherm with a R^2 value close to 1 and indicates a monolayer formation on the PTFE surface probably by adsorbing the tailgroup on the surface. Initially the adsorption density increases linearly with the equilibrium concentration, i.e., it follows Henry's law due to formation of monolayer, and ultimately reaches a plateau region at about 0.38 mM equilibrium concentration. Whereas for SDBS, both the models are almost equally fitted with an R^2 value above 0.94. For CPB there is a significant difference between the two isotherms with a higher

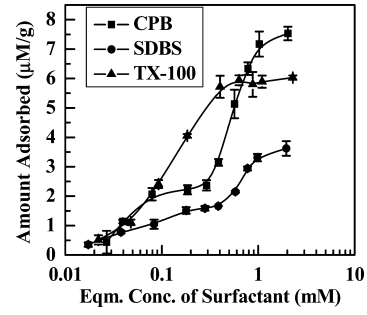

Figure 3. Adsorption isotherms of CPB, SDBS, and TX-100 on PTFE powder.

Table 2. Parameters of Langmuir and Freundlich Isotherm Equations

	Langmuir			Freundlich		
surfactant	q_m (μM·g^{-1})	$b \times 10^{-3}$ (mM^{-1})	R^2	a (μM·g^{-1})	n	R^2
TX-100	6.622	0.301	0.990	6.382	1.879	0.848
CPB	10.101	0.18	0.895	6.309	1.647	0.914
SDBS	4.115	0.048	0.946	2.99	2.141	0.96
CPB + NaCl	10.638	0.462	0.971	8.260	2.469	0.939
CPB + Na_2SO_4	12.5	0.357	0.891	7.638	2.604	0.858
SDBS + NaCl	14.285	1.190	0.987	13.031	2.164	0.924

R^2 value (~0.914) for Freundlich type. The ζ potential of PTFE particles show that the surface is having low negative charge, −4.82 mV, indicating it is mostly hydrophobic in nature, so we are expecting the majority of SDBS and CPB molecules also adsorb through the tailgroup. The shape of the isotherm indicates the sudden change in adsorption amount is more sharp for CPB than SDBS and may be due to formation of hemimicelle. To support the higher hemimicellar aggregation number for CPB we have also calculated the hemimicellar aggregation number according to Gao et al.[27] for both the surfactants and found the values are ~4 and ~2 for CPB and SDBS, respectively. So the aggregation of SDBS is not significant. In summary, we conclude SDBS isotherm follows mainly Langmuir type isothem and the similar fitting with Freundlich type model may be due to a small experimental error in the isotherm. The formation of hemimicelle on PTFE surface by the cationic surfactant (CTAB) is also reported by Dixit et al.[15] and Vanjara and Dixtit,[14] with an aggregation number 7. For the isotherms with hemimicelle formation at low surfactant concentration, amount adsorbed increases with the concentration and reaches an intermediate plateau reagion due to the saturation of monolayer, then with further increases in concentration there is a sudden rise in amount adsorbed due to the formation of hemimicelle. The critical concentration where hemimicelle formation occurs is called critical hemimicellar concentration (CHMC). In general, the driving force of hemimicelle formation is the hydrophobic interaction between the surfactant chains. At low concentration, however, the solution activity of the surfactant may not be sufficient to form any aggregation at the interface, thus the surfactants are still adsorbed as monomers. Above the CHMC the concentration of surfactants in solution is sufficient for formation of hemimicelle due to attraction of adsorbed molecule and the molecules present in the solution. The CHMC found from the isotherm is about 0.38 mM for CPB. The adsorption of three synthetic surfactants on PTFE surface may be predominated by hydrophobic interaction and there may be some other interactions such as electrostatic attraction, hydrogen bonding, and dispersion forces. There is a difference in amount adsorbed between these two ionic surfactants, having higher adsorption density for CPB. This may be attributed in terms of longer chain length of CPB than SDBS. In addition, as the surface is little negatively charged there will be repulsion between the SDBS molecules and the surface; whereas, there will be attraction between that of CPB and the solid surface. Ultimately, some CPB may also adsorb through the headgroup on the negatively charged sites and some on the hydrophobic sites through the tailgroup, finally they are also forming hemimicelle on the surface. These may be the reasons the adsorption of CPB is more than SDBS.

3.3. Effect of Electrolytes. 3.3.1. Effect of Electrolytes on CMC. The solution property of surfactants also plays a major role in the adsorption behavior at the solid−liquid interface. Effects of three different salts NaCl, Na_2SO_4, and $CaCl_2$ on solution property and adsorption behavior of SDBS and CPB are studied here. Before studying the adsorption behavior in the presence of electrolytes we have studied the change in surface tension for a particular surfactant concentration with increasing electrolyte concentration as shown in Figure 4a and b. When the surface tension becomes constant we assume CMC is reached at that particular surfactant and electrolyte concentration. The CMCs of CPB and SDBS are 0.9 and 1.5 mM, respectively, in the absence of electrolytes. In the presence of electrolytes CMC was reached at concentration far below that of the original CMC, depending on the concentration of the electrolytes, as charge screening of the ionic surfactants headgroups and close packing of the surfactants occur at the air−liquid interface. Thus, inorganic salts have a significant impact on the adsorption of ionic surfactants at air−water as well as that in solid−water interfaces. According to the Schulze−Hardy rule, the charge screening efficiency or ability to reduce the debye length of a multivalence ion is much more than a monovalence, so to get same CMC the required concentration of a multivalence salt required is significantly less than a monovalence. Table 3 shows the concentration of electrolytes required for getting CMCs of SDBS and CPB of 0.05 and 0.1 mM, respectively. SDBS and CPB have surface tension values at CMC in the absence of electrolytes 36.51 and 37.14 mN/m, respectively. The surface tension values of starting surfactant concentrations (0.05 mM and 0.1 mM) for SDBS and

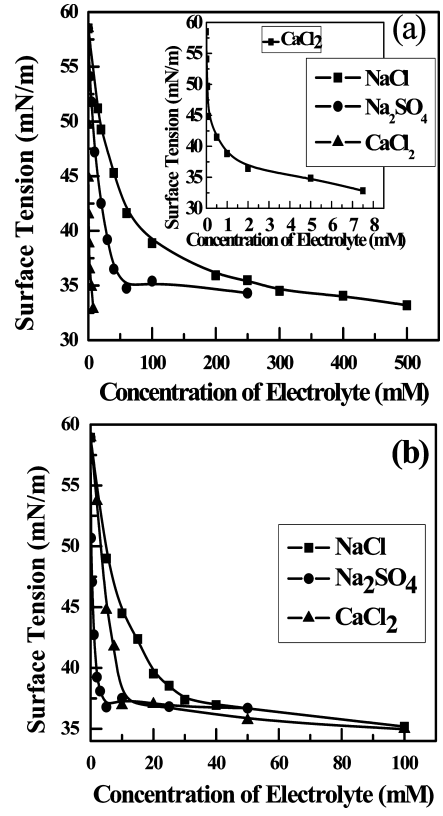

Figure 4. Surface tension reduction of surfactants solution in the presence of electrolytes: (a) SDBS, (b) CPB.

Table 3. Concentration of Electrolytes for Reaching the CMC at a Particular Concentration of SDBS and CPB, and Their Surface Tension (γ) Values at Initial Concentration and at CMC

	SDBS (0.05 mM)		CPB (0.1 mM)	
electrolytes	electrolyte concn. (IS)	γ (mN/m), initial value 58.50	electrolyte concn. (IS)	γ (mN/m), initial value 58.92
NaCl	200 mM (IS = 200)	35.94	30 mM (IS = 30)	37.39
Na_2SO_4	60 mM (IS = 180)	35.26	5 mM (IS = 15)	36.79
$CaCl_2$	2 mM (IS = 6)	36.25	10 mM (IS = 30)	36.91

CPB are 58.50 and 58.97 mN/m, respectively. Table 3 shows surface tension values reached at CMC in the presence of electrolytes are very close to that of CMC in the absence of electrolytes. From the table it is clear that for CPB when the counterion is monovalence but co-ion is not monovalence a particular CMC value is reached when the ionic strengths (IS) of the electrolyte solutions are similar, for SDBS there is a little difference but it is close to the expected value (66 mM). In contrast, when the bivalence counterion is there for SDBS the concentration required is very close to that calculated according to Schulze−Hardy rule (according to this rule $CaCl_2$ concentration required is $200/2^6 = 3.12$ mM). Whereas, CPB in the presence of bivalence counterion does not follow this rule, the concentration required is less than that of electrolyte having monovalence counterion but more than that according to Schulze−Hardy rule ($30/2^6 = 0.468$ mM).

3.3.2. Electrolytes Effect on SDBS Adsorption at a Constant Concentration. Figure 5a and b shows the effect of electrolytes on adsorption of SDBS using a constant initial surfactant concentration at PTFE surface below and above the saturation. In this study a constant surfactant concentration (0.05 mM) is used and the electrolytes concentrations are increased to see the change in adsorption. From Figure 5a, it is found that for all three electrolytes there is a linear increase in amount adsorbed with the increase in ionic strength of the electrolyte solution, with a correlation coefficient ~0.99 for all the three cases. First, we have done the adsorption study up to the electrolyte concentration where the CMC reached that particular surfactant concentration from the surface tension plot (Figure 4a, b), and found until that concentration there is no saturation in adsorption. This can be attributed as the initial concentration is constant in the presence of higher electrolyte concentration more surfactant molecules are getting adsorbed and ultimately the equilibrium concentration becomes still below the CMC at that electrolyte concentration, as a result, in this case we need to go to electrolyte concentration of far above than that shown in Table 3, to get the plateau. Figure 5b shows that with further increasing the concentration of electrolytes there indeed is a plateau level reached when the total surface of PTFE is covered. It is also worthy to observe that the maximum amount adsorbed at the plateau is very close for the three electrolytes, and that the amount is less than the plateau of the original adsorption isotherm in the absence of electrolytes above the CMC. It may also be interesting to note, at a constant surfactant concentration the effect of electrolytes show similar effect on amount adsorbed to that of increasing surfactant concentration, but in contrast, their nature of the curves are totally different. In the presence of electrolyte, there is a stiff linear rise in amount adsorbed until below the CMC then reached to a saturation level. From the linear fitting of the experimental data (ionic strength vs amount adsorbed) we found the increasing order of the slopes are $Na_2SO_4 < NaCl \ll CaCl_2$. In the presence of $CaCl_2$ the slope is 1 order of magnitude higher than those of the other two electrolytes. Quantitatively the slope in the presence of $CaCl_2$ is 35.87 times higher than that of Na_2SO_4 and 32.16 than NaCl. As we have mentioned before, since the surface is almost hydrophobic, adsorption may occur by the hydrophobic attraction between the tailgroup and the solid surface, in this situation reduction in headgroup repulsion or screening of headgroup charge in the presence of electrolyte is responsible for adsorption enhancement. The presence of bivalence counterion (Ca^{2+}) can effectively reduce the surface charge of the headgroup and show highest slope. Between NaCl and Na_2SO_4 bivalence co-ion has a negative effect on adsorption, so the slope is a little less in the presence of Na_2SO_4.

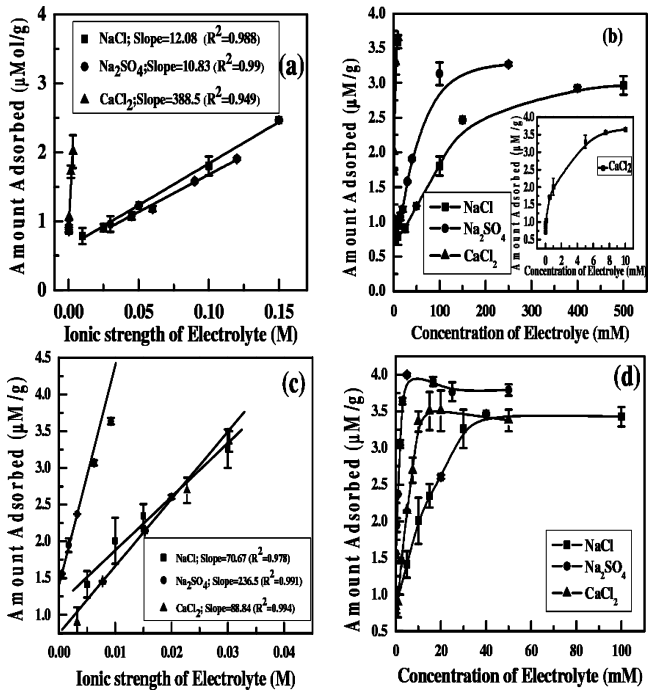

Figure 5. (a) Linear increase of SDBS amount adsorbed with the increase in ionic strength of electrolyte solutions. (b) Plateau level of SDBS adsorption in the presence of different electrolytes solutions at higher concentration. (c) Linear increase of CPB amount adsorbed with the increase in ionic strength of electrolyte solutions. (d) Plateau level of CPB adsorption in the presence of different electrolytes solutions at higher concentration.

3.3.3. Electrolytes Effect on CPB Adsorption at a Constant Concentration. Figure 5c and d shows the adsorption behavior of CPB in the presence of electrolytes using a constant surfactant concentration below and above the saturation level, respectively. From the figure it can be seen that similar natures of the curves are obtained for CPB and SDBS. Figure 5c shows similar to SDBS there is a linear increase in the amount adsorbed with the increase in ionic strength of electrolytes solutions until below the CMC. The increasing orders of the slopes of the linear lines in the presence of electrolytes are $NaCl < CaCl_2 \ll Na_2SO_4$. The slope in the presence of Na_2SO_4 is 2.65 times higher than that of $CaCl_2$ and 3.34 times than that of NaCl. So, similar to the previous study the rate of increase in adsorption is more when bivalence counterion is present than that of monovalence and less when bivalence co-ion is present. Comparing with the SDBS results we can also conclude the slope change is more sensitive to anionic surfactant and bivalence counterion com-

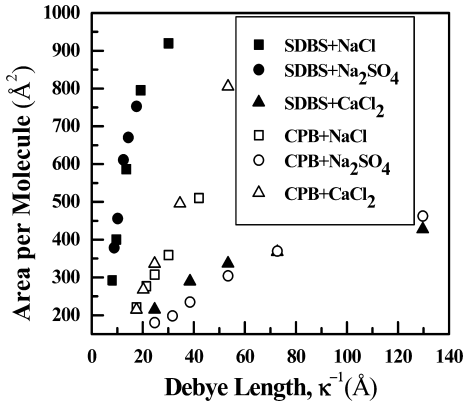

Figure 6. Area occupied per molecule of SDBS and CPB surfactants vs Debye length, κ^{-1} (Å). Areas occupied per molecule in absence of electrolyte are 996.40[2] and 859.37 Å^2 for SDBS and CPB, respectively.

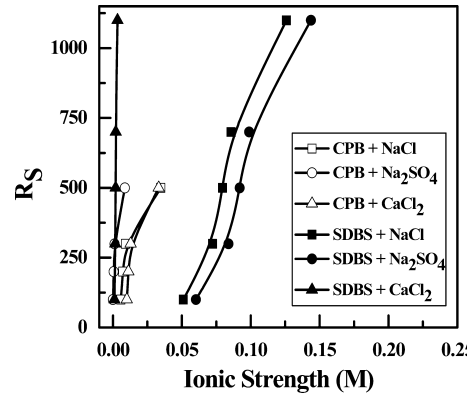

Figure 7. Reduction of surfactant consumption (R_S) with the increase in ionic strength of electrolyte solutions.

bination rather than with cationic surfactant. The above results indicate the decrease in the electrostatic repulsion between the surfactant headgroups is the main mechanism here to increase the amount adsorbed due to closer packing at the surface. Figure 5d shows the amount adsorbed at the plateau is similar for NaCl and $CaCl_2$ and the difference is not significant from that in the presence of Na_2SO_4. Similar to anionic surfactants it can be seen that the maximum amount adsorbed is lower than that plateau of the isotherm in the absence of electrolyte. Since the amount adsorbed increases linearly and then reaches a plateau level, probably the monolayer formation is there in this surfactant concentration with a closer packing in the presence of electrolytes. In the earlier publication it was reported that during the adsorption of cationic surfactant in the presence of electrolytes on a hydrophilic surface the reduction in headgroup repulsion is important for adsorption enhancement.[25]

3.3.4. Area Occupied Per Molecule in the Presence of Electrolytes. Debye length (κ^{-1}), defined as the inverse of the Debye−Huckel parameter, is the measure of screening of the electrical double layer in the presence of electrolyte. The Debye−Huckel parameter is represented as

$$\kappa = \left[\frac{1000e^2N_A}{\varepsilon_r\varepsilon_0 k_B T}\sum_i z_i^2 C_i\right]^{1/2} \tag{10}$$

where e is the elementary charge, N_A is Avogadro's number, ε_r is the dielectric constant, ε_0 is the permittivity in vacuum, k_B is the Boltzmann constant, T is the absolute temperature, and z_i and C_i are the valence and molar concentrations of ionic species i, respectively. The area per molecule is calculated as

$$A_m = \frac{S \times 10^{26}}{\Gamma N_A} \tag{11}$$

where A_m is the area occupied per surfactant molecule in Å^2, S is the specific surface area of PTFE in m^2 g^{-1}, and Γ is the amount of surfactant adsorbed at saturation in μmol·g^{-1}. From Figure 6, it can be seen that the area occupied per SDBS molecule linearly increases with the increase in Debye length. It is also found that the area occupied is very similar for a particular Debye length in the presence of NaCl and Na_2SO_4 but different for $CaCl_2$, especially at higher Debye length. For a constant Debye length the area occupied per SDBS molecule is less in the presence of $CaCl_2$ than in the presence of NaCl or Na_2SO_4. Figure 6 also shows a similar type of observation obtained for CPB. The area occupied per CPB molecule linearly increases in the presence of electrolytes and is almost similar with the variation of Debye length when the electrolytes have monovalence counterion. In the presence of bivalence counterion (SO_4^{2-}) the area occupied per CPB molecule is less and the difference from the monovalence counterion is more at higher Debye length. This similar behavior for both the anionic and cationic surfactants is mainly due to the similar adsorption pattern of the molecules at the hydrophobic solid surface. Comparisons of both the surfactants together show there is a difference between the monovalence counterions for SDBS and CPB, but when bivalence counterion is present difference in area occupied by the two surfactants is almost similar.

3.3.5. Reduction in Surfactant Concentration. Since the amount adsorbed significantly increases in the presence of electrolyte, the reduction in surfactant concentration to obtain the same amount adsorption was calculated and presented in Figure 7. For the calculation of percent reduction, first the amount adsorbed for a particular initial concentration was taken from the adsorption isotherm data and the required electrolyte concentration to reach that amount adsorbed was calculated from the linear plot of amount adsorbed vs ionic strength. The percent reduction of surfactant (R_S) was calculated according to the equation

$$R_S = \frac{(C_i - C_E)}{C_i} \times 100 \tag{12}$$

where C_i is the particular initial surfactant concentration from the isotherm, C_E is the concentration of surfactant used for study of electrolyte effect (0.05 mM for SDBS and 0.1 mM CPB). C_i was chosen in a particular range where the amount adsorbed fell in the linear range of Figure 5a and c. From Figure 7 it can be seen that there is a significant increase in R_S with the increase in ionic strength and the reduction efficiency is more for SDBS systems, especially in the presence of $CaCl_2$.

3.3.6. Effect of Electrolytes on Surfactant Adsorption Isotherm. Figure 8 represents the adsorption isotherm of CPB in the presence of 50 mM NaCl and 16.5 mM Na_2SO_4 each having equal ionic strength to study the counterion valence effect on the isotherm. The isotherms are then fitted with Langmuir and Freundlich model and the parameters are listed in Table 2. From the table it is observed that for both the cases Langmuir isotherm fits better than Freundlich isotherm. In the presence of electrolytes the negative surface charge of PTFE surface may be reduced further, as a result the surfactants are mostly adsorbing like a uniform hydrophobic surface. That may be the reason why the isotherm is shifted from Freundlich to Langmuir type. The increase in amount adsorbed in the plateau region is mainly due to reduction in headgroup repulsion as explained

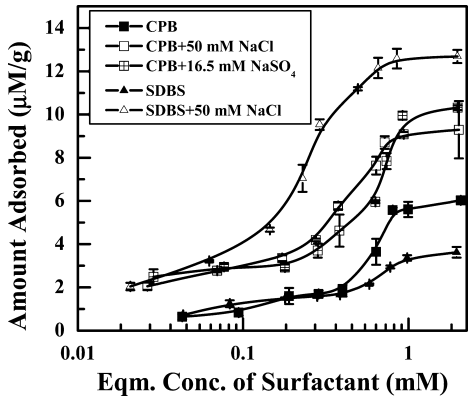

Figure 8. Adsorption isotherms of CPB, CPB + 50 mM NaCl, CPB + 16.5 mM Na_2SO_4, SDBS, and SDBS + 50 mM NaCl on PTFE powder.

before. Higher adsorption amount in the presence of Na_2SO_4 shows counterion valence effect is more important, although the ionic strength is the same. Throughout the isotherm since the ionic strength is constant the difference in amount adsorbed between NaCl and Na_2SO_4 is less.

Figure 7 also depicts the adsorption isotherm of SDBS without electrolyte and at 50 mM NaCl. For SDBS we have not studied the effect of $CaCl_2$ due to formation of precipitate at 16.5 mM concentration. Similar to CPB adsorption isotherm of SDBS also shows better fitting with Langmuir model may be due to similar reason. The amount adsorb increased also due to further decrease in surface potential and also reduction in headgroup repulsion between the adsorbed molecules. The adsorption of pure surfactants show CPB has higher adsorption capacity than SDBS, whereas in the presence of NaCl the trend is reversed. This observation can be attributed in the following ways: (i) in the presence of NaCl for CPB when the surface charge is reduced, the number of molecules adsorbed due to oppositely charged surface is reduced, and the adsorption enhancement is only due to the reduction in headgroup repulsion; (ii) for SDBS adsorption, the repulsion between same charged surface and headgroup is reduced, which is favorable for adsorption in addtion to reduction in headgroup repulsion. As a result, SDBS shows higher adsorption capacity at the plateau level in the presence of NaCl than that of CPB.

4. Conclusion

The rate of adsorption of three synthetic surfactants TX-100, SDBS, and CPB on PTFE surface is very fast; within 10 min the equilibrium is reached. Pseudo-second-order kinetic model fits well for the adsorption kinetics of all three surfactants with the following order of rate constant values with a minimum difference: CPB > TX-100 > SDBS. The adsorption isotherms of TX-100 show Langmuir type but SDBS and CPB are better fit with Freundlich type model. In the presence of electrolytes, isotherms of both the ionic surfactants show better fitting with Langmuir type isotherm. When the initial concentration of the ionic surfactant is constant and far below the CMC, the addition of electrolytes shows there is a linear relationship between the amount of surfactant adsorbed and ionic strength of the electrolyte solutions. The increasing order of the slopes in the linear portion for SDBS is $Na_2SO_4 < NaCl \ll CaCl_2$, and that for CPB is $NaCl < CaCl_2 \ll Na_2SO_4$. The area occupied per molecule (A_m) also changes linearly with the Debye length in the presence of electrolytes for both the ionic surfactants. The A_m is mainly dependent on Debye length but independent of the types of electrolytes when monovalence counterion is present. Whereas in the presence of bivalence counterion, for a particular Debye length the difference in A_m is observed. The difference in A_m in the presence of mono- and bivalence counterion is more at higher Debye length. The main mechanism of increase in amount adsorbed for both the surfactants can be attributed to the decrease in the electrostatic repulsion between the surfactant headgroups, and as a result, closer packing of the surfactant molecules at the surface.

This study gives an idea about the adsorption behavior of anionic and cationic surfactants on a hydrophobic surface in the presence of electrolytes. The study may be useful in some applications such as wetting, colloid stability, and dispersion of polymers, etc., where surfactant adsorption is an important parameter; moreover, surfactant consumption can also be reduced by adding small amount of electrolytes to the surfactant solutions.

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Wetting of TX-100 and Igepal CO-630 Surfactants on a PTFE Surface

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Supporting Information

ABSTRACT: Nonionic surfactants are advantageous in a diversified range of applications from household cleaners, laundry detergents, and shampoo to paints, coatings, and food emulsifiers because of their low CMC and surface tension values over the ionic surfactants. Nonionic surfactants, in general, are very useful in mixed surfactant systems because of their electrical neutrality. Among the similar class of nonionic surfactants, structural difference is important in the performance. In this study, we report on the adsorption and wetting behavior of two nonionic surfactants (TX-100 and Igepal CO-630) having the same head group but structurally different tail groups. The kinetics of adsorption follows a pseudo-second-order kinetic model and a Langmuir-type isotherm for both the surfactants. The change in contact angle with the concentration of surfactant follows a trend similar to that for adsorption onto a PTFE surface. At low surfactant concentration, Igepal CO-630 shows a slightly higher adsorption density and better wetting properties than TX-100. Both surfactants show lower adsorption densities at the PTFE−water interface than at the air−water interface.

1. INTRODUCTION

The wetting of hydrophobic surfaces by surfactant solutions is very important in surface and interface science, owing to the fact that many industrial processes and daily life applications are impossible to consider without wetting. In the wetting process, adsorption of surfactant at the solid−liquid interface and surface tension at the air−liquid interface plays an important role. Because hydrophobic surfaces have very low surface energies, wetting with a polar solvent is difficult and can be enhanced using surfactants. Surfactants having low surface tension values at the critical micellar concentration (CMC) and low solid−water interfacial tension upon the adsorption of surfactants always show better wetting properties.

In view of the widespread applications of wetting phenomena, many researchers have studied the wettability of different types of hydrophilic and hydrophobic surfaces by different single surfactants,[1,2] mixed surfactant systems,[3−5] and additives.[6,7] In mixed surfactant systems, mixtures of similar cationics[3] and nonionics[5] and dissimilar mixtures of both cationic and nonionic surfactants[4,8] have been studied. The effects of different additives such as alcohols[6,9−12] and electrolytes[7] have also been studied thoroughly.

In general, nonionic surfactants are preferable in many applications because of their biocompatibility, lower sensitivity toward electrolytes, low CMC and surface tension values compare to those of ionics, and so on. For a long time, many researchers have studied the wetting behaviors of nonionic surfactants on both hydrophilic and hydrophobic surfaces for different applications.[2,13−19] Mostly, the wetting properties increase in the presence of nonionic surfactants for both hydrophilic and hydrophobic surfaces. The wetting properties also depend on the molecular structure of the surfactant,[20] as well as the nature of hydrophilic and hydrophobic groups of different surfactants. The wetting properties of a nonionic surfactant can also be improved using alcohols of different chain lengths,[21] binary mixtures,[4,5,22,23] and ternary surfactant mixtures (two nonionic + one ionic).[24]

The present study focuses on the adsorption and wetting behaviors of two nonionic surfactants (TX-100 and Igepal CO-630) having similar head groups but dissimilar tail groups on a polytetrafluoroethylene (PTFE) surface. The surfactants have similar head groups, nine ethylene oxide groups attached to a benzene ring, but a structural difference in the tail groups. Igepal CO-630 and TX-100 contain *n*-nonyl (C_9) and an eight-carbon branched chain (C_8) hydrocarbon (1,1,3,3-tetramethylbutyl), respectively, as the tail group. The adsorption behavior of the surfactants between the PTFE−water and air−water interfaces obtained from the wetting study were also compared with the results of independent adsorption studies at those respective interfaces. To the best of our knowledge, this type of study has not been reported before. TX-100 and Igepal CO-630 were chosen because they are members of the typical alkyl polyethylene oxide category widely used in several practical applications. Moreover, from the environmental viewpoint, straight-chain hydrophobic groups are more important because of their biodegradable nature than branched chains in a nonionic surfactant.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Polytetrafluoroethylene (PTFE) slides of dimensions 25.34 mm × 1.12 mm were cut from a sheet purchased from J. Khushal Das and Co., Mumbai, India, and the powder used for adsorption experiments was purchased from Pragati Plastics Pvt. Ltd., Delhi, India. Triton X-100 (TX-100) [*p*-(1,1,3,3-tetramethylbutyl)phenyl ether polyethylene glycol) and Igepal CO-630 (polyoxyethylene nonylphenol) were purchased from Sigma-Aldrich Gmbh, Munich, Germany (technical

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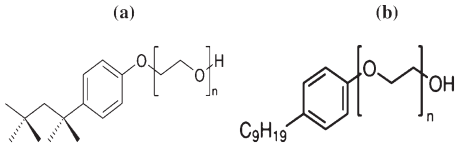

Figure 1. Structures of (a) Triton X-100 and (b) Igepal CO-630 ($n = 9$).

grade, catalog nos. 93418 and 542334) and used without any further purification. The structures of the surfactants are shown in Figure 1. Ultrapure water (Sartorius, Göttingen, Germany) of 18.20 MΩ cm resistivity, 71.50 mN/m surface tension, and 6.5−7.0 pH was used for all the experiments. The particle size of the PTFE powder was measured using a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., Malvern, U.K.), and the average particle size was found to be 115.70 μm. The zeta potential (ζ) of PTFE powder was measured in the presence of 0.01 mol KCl solution using a Zetasizer Nano ZS instument (Malvern Instruments Ltd., Malvern, U.K.) and found to be −4.82 mV. The specific surface area [Brunauer−Emmett−Teller (BET)] of the PTFE powder was measured by N_2 adsorption−desorption studies at liquid nitrogen temperature (−195.80 °C) using an Autosorb-1 instrument (Quantachrome Instruments, Boynton Beach, FL) and found to be 4.34 m^2/g.

2.2. Measurement of Surface Tension and CMC. All surfactant solutions were prepared freshly just before the measurements. The solutions of desired concentration were prepared from a 10 mmol/L stock solution using a 100 mL volumetric flask. The surface tensions of aqueous surfactants solutions (0.0005−2 mmol/L) were measured by the Wilhelmy plate method using a surface tensiometer (DataPhysics, Filderstadt, Germany, DCAT-11EC) at 25 ± 0.5 °C, with the temperature maintained using an external constant-temperature water circulator. The motor speed was 1 mm/s, and the immersion depth of the platinum plate in the surfactant solution was maintained at 3 mm. After measurement of each concentration, the plate was cleaned with water and acetone and then burned in an alcohol flame. The CMCs of Triton X-100 (TX-100) and Igepal CO-630 were found to be 0.15 and 0.08 mmol/L, respectively, by the surface tension measurement technique.

2.3. Surfactant Adsorption Kinetics and Isotherm of on a PTFE Surface. For the adsorption experiments, a volume of 10 mL of surfactant solution having different concentrations (0.025−2 mmol/L for the isotherms and 0.05 mmol/L for kinetics) were taken in 60 mL plastic bottles, and 0.1 g of PTFE powder was added in each case. The bottles were shaken well for 2 h at 25 ± 0.5 °C on an incubator shaker. PTFE particles were separated from the mixture by centrifugation at 5000 rpm. The concentrations of the surfactant solutions before and after adsorption were determined by UV−vis spectrophotometer (UV-3600, Shimadzu, Kyoto, Japan) using their respective calibration curves (absorbance versus concentration) constructed from known concentrations. The experiments were repeated at least three times, and the average data were plotted. The amount of surfactant adsorbed was determined from the equation[25]

$$\Gamma = \frac{(C_i - C_{eq})V}{m \times 1000} \quad (1)$$

where C_i and C_{eq} are the initial and equilibrium concentrations (mmol/L), respectively; V is the volume of surfactant solution (mL); and m is the mass of adsorbent (g).

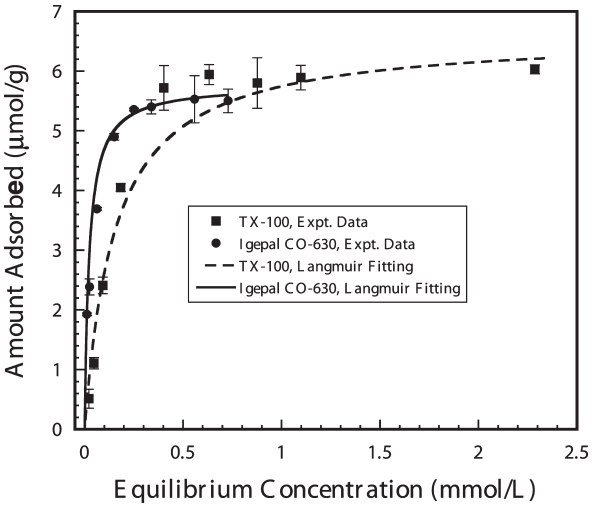

Figure 2. Adsorption isotherms of TX-100 and Igepal CO-630 on PTFE powder.

2.4. Measurement of Contact Angle. The dynamic advancing (θ_A) contact angle was measured by the Wilhelmy balance method using the above-mentioned surface tensiometer. All experiments were carried out at constant temperature (25 ± 0.5 °C). A motor speed of 0.2 mm/s and an immersion depth of the PTFE plate of 5 mm were maintained during the contact angle measurements. A good-quality PTFE plate was chosen and washed several times with first acetone and then ultrapure water to remove impurities. The plate was then dried under blowing hot air. The same procedure was repeated after the measurement of each surfactant concentration.

3. RESULTS AND DISCUSSION

3.1. Surfactant Adsorption Isotherm on a PTFE Surface. The adsorption isotherm was also determined to see the difference in amounts adsorbed at equilibrium in a range of concentrations from below to above the CMC for both surfactants. Figure 2 presents the adsorption isotherms of the two nonionic surfactants on a PTFE surface. Because of the chemical inertness of the low-energy hydrophobic solid surface, chemical interaction with the surfactant is minimal. From the figure, it is clear that the natures of the adsorption isotherms for TX-100 and Igepal CO-630 are similar and are of Langmuir type. Initially, at low equilibrium concentration, because of the presence of more free accessible sites, the isotherm rises linearly with a higher slope, whereas at higher equilibrium concentration, the formation of a plateau region indicates monolayer coverage of the surfactants on the PTFE surface because of the negligible intermolecular interaction between the adsorbed surfactant molecules. Comparison between the two isotherms shows that, at low surfactant concentrations, the amount adsorbed for Igepal CO-630 is higher than that for TX-100, which might be due to the bulkiness of the TX-100 molecule. In contrast, at the plateau level, TX-100 has a slightly higher amount adsorbed, although the change is not very significant.

Both isotherms were fitted with the Langmuir and Freundlich models, and better fits were found with the Langmuir model. The linear forms of the Langmuir and Freundlich isotherms are

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Table 1. Parameters of the Langmuir and Freundlich Isotherm Models

	Langmuir			Freundlich		
surfactant	q_m (μmol g^{-1})	b (μmol^{-1})	R^2	a (μmol g^{-1})	n	R^2
TX-100	6.62	6.56	0.99	6.38	1.87	0.84
Igepal CO-630	5.78	43.25	0.99	6.99	3.70	0.92

given by[26,27]

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2)$$

$$\log q_e = \log a + \frac{1}{n}\log C_e \quad (3)$$

respectively, where q_m is the equilibrium amount adsorbed (μmol g^{-1}), b is the adsorption constant of the Langmuir equation (μmol^{-1}), C_e is the equilibrium concentration of surfactant in solution (mmol/L), a is a constant or coefficient of the Freundlich isotherm equation representing the adsorption capacity, and n is a constant (reciprocal of the exponent of the Freundlich isotherm equation). Values for the parameters are listed in Table 1.

3.2. Surfactant Adsorption Kinetics on a PTFE Surface. Because adsorption is inherently associated with the wetting process, the adsorption kinetics was studied to determine the equilibrium time, as well as the rates of adsorption of the two different nonionic surfactants (TX-100 and Igepal CO-630) from a solution with an initial concentration of 0.05 mmol/L on a PTFE surface in a batch study. The data on the kinetics of adsorption are shown in Figure 3, from which it is clear that the rate of adsorption is very high for both surfactants, with equilibrium times of approximately 10 min for TX-100 and 5 min for Igepal CO-630 and a higher adsorption amount for Igepal CO-630. As the surface is mostly hydrophobic, adsorption of these nonionic surfactants occurs by attachment of the tail group through van der Waals forces.

Now, to calculate the rate constant of the process, the experimental results were fitted with pseudo-first-order and pseudo-second-order models, and better fits were found for the second-order model using the linear form of the equation.[25]

Pseudo-first-order kinetics can be expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

and pseudo-second-order kinetics can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (5)$$

where q_t and q_e are the amounts (μmol/g) of surfactant adsorbed at time t and at equilibrium, respectively, and k_1 (min^{-1}) and k_2 [g/(μmol min)] are the adsorption rate constants for the pseudo-first-order and pseudo-second-order models, respectively. The adsorption rate constants of both models calculated by eqs 4 and 5 are reported in Table 2.

For both surfactants, the correlation coefficient for fitting (R^2) was found to be close to 1, with second-order adsorption rate constants of 0.91 and 2.09 g (μmol min)$^{-1}$ for TX-100 and Igepal CO-630, respectively. The high R^2 values obtained from the kinetic plots suggest that adsorption of surfactants on a PTFE surface can be better expressed by the pseudo-second-order model, as shown in Figure 3, having a higher R^2 value (>0.99) than the pseudo-first-order model. From the data, it is clear that, at a constant surfactant concentration, the rate of adsorption is higher for Igepal CO-630 than for TX-100, which might be due to the presence of a straight-chain hydrophobic tail group in Igepal CO-630.

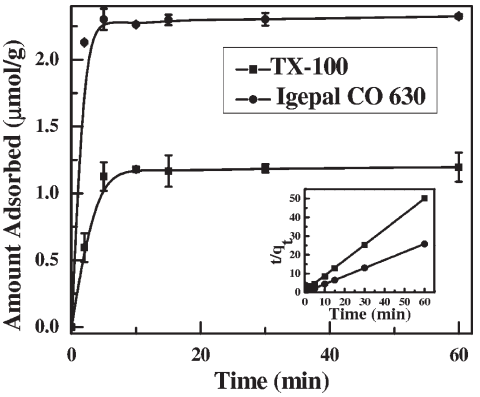

Figure 3. Adsorption kinetics of TX-100 and Igepal CO-630 on PTFE powder. Inset shows linear fitting of pseudo-second-order kinetics.

3.3. Area Occupied per Surfactant Molecule at the PTFE−Water Interface. From the maximum adsorption capacity, the molecular density or the adsorption density of the surfactants can be expressed in terms of the effective area occupied per surfactant molecule at the PTFE−water interface. Assuming that monolayer adsorption occurs at the PTFE−water interface area, the occupied per molecule can be calculated as[28]

$$a_m = \frac{1}{N_A \Gamma_{SL}} \quad (6)$$

$$\Gamma_{SL} = \frac{q_m}{S_{BET} \times 10^6} \quad (7)$$

where a_m is area occupied per molecule (nm^2), Γ_{SL} is the surface excess concentration of surfactant (mol/m^2) at the PTFE−water interface, q_m is the amount of surfactant adsorbed on the PTFE surface (μmol/g) calculated from the Langmuir adsorption isotherm equation, S_{BET} is the BET surface area of the PTFE powder (m^2/g), and N_A is Avogadro's number (6.02×10^{23}). The values for the area occupied per molecule obtained from the above equations for TX-100 and Igepal CO-630 are 1.09 and 1.24 nm^2, respectively.

3.4. Change in Contact Angle with the Surfactant Concentration. The change in advancing contact angle on the PTFE surface was studied and is plotted in Figure 4. Figure 4 shows that there is a gradual decrease in contact angle with increasing surfactant concentration until 0.1 mmol/L (log C = −1) for Igepal CO-630 and 0.3 mmol/L (log C = −0.5) for TX-100; beyond that concentration, the contact angle remains constant. The contact angle changes from 117.14° (pure water) to 80.42° with increasing concentration of TX-100; similarly, for Igepal CO-630, the change is from 117.14° to 82.79°. Thus, for both surfactants, the contact angle decreases until close to the CMC. The contact angles are similar for the two surfactants, with a slightly lower value for Igepal CO-630 below the CMC region, although the final saturation value is ∼2° lower for TX-100. Comparison of these plots with the adsorption isotherm reveals some similarities, such as that the amount of Igepal CO-630 adsorbed is also higher at low concentration and that, near the

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Table 2. Pseudo-First-Order and Pseudo-Second-Order Kinetic Parameters

	pseudo-first-order kinetics			pseudo-second-order kinetics		
surfactant	k_1 (min^{-1})	q_e (μmol/g)	R^2	k_2 [g (μmol min)$^{-1}$]	q_e (μmol/g)	R^2
TX-100	0.11	0.19	0.61	0.91	1.21	0.99
Igepal CO-630	0.04	0.08	0.35	2.09	2.33	1

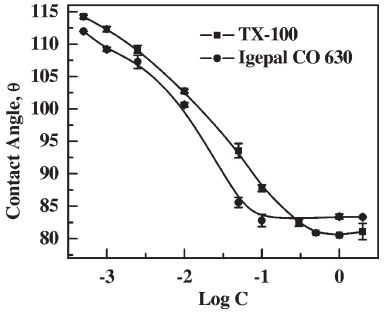

Figure 4. Change in contact angle (θ) with concentration (log C) for different surfactants.

CMC, TX-100 shows a slightly higher adsorption value at the plateau level, although the difference is not significant. This result can be explained as being due to a close relationship between the decrease in contact angle on the PTFE surface and the adsorption density. As mentioned before, this behavior might be due to the presence of the straight-chain tail in Igepal CO-630 resulting in a higher adsorption density at lower concentration as well as a greater lowering of the contact angle.

3.5. Surface Excess at the PTFE−Water and Air−Water Interfaces. Similarly to the adsorption of surfactants at the solid−liquid interface, that at the air−liquid interface is also important in the wetting process. Adsorption of a surfactant at a solid−liquid interface contributes to the wetting process by changing the hydrohilicity/hydrophobicity or the surface energy. Likewise, adsorption of a surfactant at an air−liquid interface changes the surface tension, which is similar to the surface energy at the air−liquid interface. The contact angle can be related to the surface or interfacial tensions using Young's equation as

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \quad (8)$$

where γ_{SL}, γ_{LG}, and γ_{SG} are the interfacial tensions at the solid−liquid, air−liquid, and solid−gas interfaces, respectively. The amount adsorbed or the surface excess (Γ_{LG}) at the air−liquid interface (mol/m^2) can be calculated as

$$\Gamma_{LG} = -\frac{1}{2.303RT}\frac{d\gamma_{LG}}{d \log C} \quad (9)$$

where R is the universal gas constant [8314 m^3 Pa/(kg mol K)], T is the absolute temperature, and N_A is Avogadro's number (6.02×10^{23}). Similarly, the surface excess at the other two interfaces (Γ_{SG} and Γ_{SL}) can also be calculated. Rearranging the surface excess equations for the three interfaces and substituting eq 8 gives the Lucassen−Reynolds equation[29,30]

$$\frac{\Gamma_{SG} - \Gamma_{SL}}{\Gamma_{LG}} = \frac{d(\gamma_{SG} - \gamma_{Sl})}{d\gamma_{LG}} = \frac{d\gamma_{LG} \cos \theta}{d\gamma_{LG}} \quad (10)$$

The surface excess at the solid−gas interface can be assumed to be zero ($\Gamma_{SG} \approx 0$). The ratio of Γ_{SL} to Γ_{LG} can be obtained from the slope of a plot of $\gamma_{LG} \cos \theta$ (adhesional tension) versus γ_{LG}. If the slope of the curve (Γ_{SL}/Γ_{LG}) is −1, then the surface excesses at the solid−liquid and air−liquid interfaces are equal. The plot of adhesional tension versus surface tension shows a linear relationship (Figure S1 of the Supporting Information) with a slope of −0.86 (R^2 = 0.98). It was also found that there was no difference between the two surfactants. This indicates that the surface excesses at the PTFE−water and air−water interfaces are not equal. To calculate the actual surface excess at the air−water interface, the surface tension of each surfactant solution was measured, and eq 6 was used to calculate the values A_{min}. The surface excess values obtained from the experimental data are also comparable with the previously reported values included in Table 3. This table shows that the values of surface excess are similar for the two surfactants. The ratios of the surface excess values between two interfaces are 0.65 and 0.58 for TX-100 and Igepal CO-630, respectively, which also confirms the inequality in surface excess at the two interfaces, in agreement with the contact angle results. The values show that there is a little difference in the Γ_{SL}/Γ_{LG} ratio between the two surfactants measured independently and that these values are lower than those obtained from the contact angle measurements. This difference can be attributed to the following causes: (i) There are differences between the different measurement techniques. (ii) The PTFE sheet and powder were obtained from different sources, which could result in variations in quality. (iii) The amounts of surfactant adsorbed on the PTFE surface are low, and the UV−vis measurement technique is not very precise, so that some experimental error could also be incurred in the adsorption experiments.

For the confirmation of equal adsorption at the solid−liquid and air−liquid interfaces, $\Gamma_{SL}/\Gamma_{LG} = -1$ is a necessary condition. At the same time, another condition should also be fulfilled: linearity of the plot of cos θ versus $1/\gamma_{LG}$ with an intercept on the cos θ axis equal to −1. The plot of our results (Figure S2 of the Supporting Information) shows that there is a linear relationship between cos θ and $1/\gamma_{LG}$ with an intercept of −0.84 (R^2 = 0.98). Finally, it can be concluded that the surface excess concentrations at the PTFE−water and air−water interfaces are not equal in this study. In this regard, there is no general rule for predicting whether the surface excesses at the solid−liquid and air−liquid interfaces will be equal; rather, it might depend on the solid surface as well as the type of surfactant. From some previously reported studies, it appears that, for low-surface-energy solids, the surface excesses at the solid−water and air−water interfaces are same;[3,10,11,32] however, other studies have also reported unequal adsorption between hydrophobic solid−water and air−water interfaces, such as nylon and poly(methyl methacrylate) (PMMA)[3,33] and PTFE.[7]

3.6. PTFE−Water Interfacial Tension and Critical Surface Tension of Wetting. From eq 8, it is clear that the PTFE−water interfacial tension is also equally important in the wetting process as the air−water interfacial tension or surface tension. For reducing the contact angle at the PTFE−water interface, reductions in both interfacial tensions are essential. Figure 5 shows the

Table 3. CMC, Surface Tension at the CMC, Surface Excess, and Area Occupied per Molecule at the Air−Water Interface for TX-100 and Igepal CO-630

surfactant	CMC (mmol/L)	γ_{CMC} (mN/m)	exp Γ_{LG} (mol/m^2 × 10^6)	exp A_{min} (nm^2)	literature Γ_{LG} (mol/m^2 × 10^6) [A_{min} (nm^2)]
TX-100	0.15	31.01	2.36	0.70	2.5 [0.66] at 25 °C[28]
Igepal CO-630	0.08	31.02	2.31	0.71	3.25 [0.51][31]

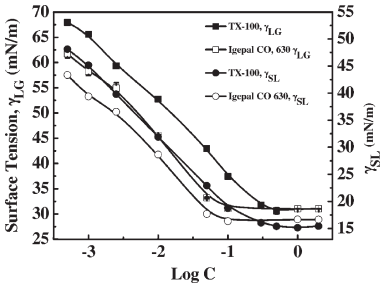

Figure 5. Change in surface tension (mN/m) and PTFE−water interfacial tension with the surfactant concentration (log C).

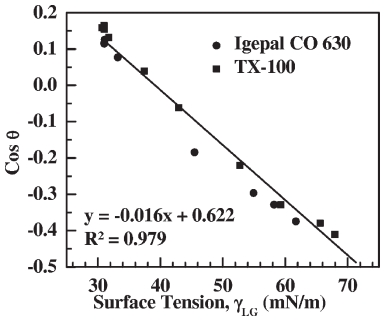

Figure 6. Plot of cos θ versus surface tension (mN/m) for different surfactants.

changes in both the interfacial tensions with log C. From the figure, it is clear that Igepal CO-630 has a slightly lower value for both the interfacial tensions than TX-100, whereas their plateau levels are almost same. The PTFE−water interfacial tension changes from 52.85 mN/m (pure water) to 15.43 and 16.36 mN/m for TX-100 and Igepal CO-630, respectively, and the surface tension value changes from 71.50 mN/m (pure water) to 31.01 and 31.02 mN/m for TX-100 and Igepal CO-630, respectively.

As in previously reported studies,[34,35] there is a linear relationship between cos θ and γ_{LG}, as shown in Figure 6. The critical surface tension (γ_C) value of 23.62 mN/m was obtained by extrapolating the curve to cos θ = 1; this value is close (23.46 mN/m) to that reported before.[5]

3.7. Work of Adhesion of Surfactant Solutions to a PTFE Surface. The work of adhesion measures the interactive force between the two different (solid and liquid) phases. The interaction between the two phases and the contact angle can be presented using the Dupree and Young−Dupree equations, respectively

$$W_a = \gamma_{LG} + \gamma_{LG} - \gamma_{SL} \quad (11)$$

$$W_a = \gamma_{LG}(1 + \cos\theta) \quad (12)$$

The work of adhesion depends on both surface tension and contact angle; for zero contact angle, $W_a = 2\gamma_{LG}$. Therefore, zero

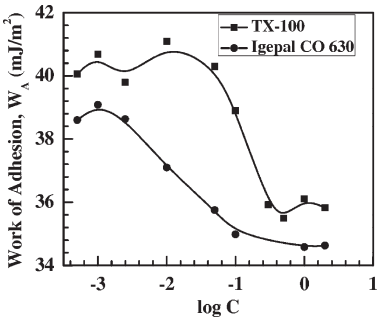

Figure 7. Change in the work of adhesion (W_a) with surfactant concentration (log C) for different surfactants.

contact angle results when the forces of attraction between liquid and solid are equal to or greater than those between liquid and liquid, and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself. The values of the work of adhesion at different surfactant concentrations are plotted in Figure 7. This figure shows that the values of W_a decrease with a slight irregularity with increasing concentration of surfactant. Igepal CO-630 has lower W_a values than TX-100. The change in W_a with surfactant concentration can also be attributed to the unequal surface excesses between the air−liquid and solid−liquid interfaces. Mathematically, this can be shown as follows. The differential form of eq 11 can be written as

$$\frac{dW_a}{d\gamma_{LG}} = \frac{d\gamma_{SG}}{d\gamma_{LG}} - \frac{d\gamma_{SL}}{d\gamma_{LG}} + 1 \quad (13)$$

From the Gibbs adsorption equation, $d\gamma_{SG}/d\gamma_{LG} = \Gamma_{SG}/\Gamma_{LG}$, and $d\gamma_{SL}/d\gamma_{LG} = \Gamma_{SL}/\Gamma_{LG}$. Assuming $\Gamma_{SG} \approx 0$ when there are equal surface excesses on the two interfaces, $\Gamma_{SL}/\Gamma_{LG} = 1$, and $dW_a/\gamma_{LG} = 0$, or W_a = constant. Therefore, it can be assumed that the work of adhesion will not change with the concentration of surfactant. As shown before, for this study, $\Gamma_{SL}/\Gamma_{LG} < 1$, or $dW_a/d\gamma_{LG} \neq 0$, which indicates that the work of adhesion will change with the concentration of surfactant.

To further analyze the results for the work of adhesion, it was observed that, although the contact angle decreases in the presence of surfactant solutions, the work of adhesion also decreases simultaneously. In general, from a basic understanding, with the decrease in contact angle, the wetting property enhances; as a result, the work of adhesion increases. This result can be attributed to the fact that, initially, the contact angle on the PTFE surface in the presence of water and low surfactant concentration is above 90°, where cos θ values are negative. As a result, the $(1 + \cos\theta)$ term increases gradually with the decrease in contact angle. At the same time, the surface tension also decreases gradually. The decrease in surface tension is greater than the increase in the $(1 + \cos\theta)$ term; as a result, the work of adhesion values decrease with increasing concentration.

3.8. Hamaker Constant for the PTFE−Water Interaction. The experimental determination of the Hamaker constant (A)

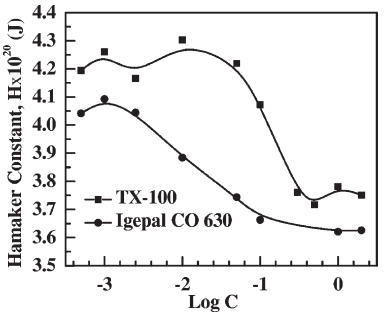

Figure 8. Change in the Hamaker constant (H) with concentration (log C) for different surfactants.

for a given material in surfactant solution can be useful for discussing the interaction between solid and liquid. When the Hamaker constant is positive ($A > 0$), it corresponds to an attraction between the molecules, and when it is negative ($A < 0$), it corresponds to repulsion. The constant of the PTFE−water system can be written as[36]

$$A_{\mathrm{PTFE-water}} = 12\pi D^2 \gamma_{\mathrm{LG}}(1 + \cos\theta) \qquad (14)$$

where D is the distance between the atoms at contact. Literature values of Hamaker constant in a vacuum for water and PTFE are $A_{\mathrm{water}} = 3.8 \times 10^{-20}$ J and $A_{\mathrm{PTFE}} = 4.4 \times 10^{-20}$ J. Applying the Bertholet relation (geometric mean approximation), the Hamaker constant for the PTFE−water system can be calculated as $A_{\mathrm{PTFE-water}} = (A_{\mathrm{water}}A_{\mathrm{PTFE}})^{1/2} = (3.8 \times 4.4)^{1/2} \times 10^{-20}$ J = 4.08×10^{-20} J. Using this $A_{\mathrm{PTFE-water}}$ value, the contact angle, and the surface tension for pure water in eq 14, one obtains D = 0.17 nm. Further, $A_{\mathrm{PTFE-water}}$ was calculated in the presence of surfactant solution and is presented in Figure 8. Similarly to the plot for the work of adhesion, there are slight irregularities at low surfactant concentrations, but at higher concentrations, there is a sharp decrease in Hamaker constant with increasing concentration, ultimately reaching a plateau region close to the CMC of the individual surfactants. Throughout the concentration range studied, Igepal CO-630 exhibited lower values than TX-100.

3.9. Wetting Free Energy of a PTFE Surface. As the energy of the PTFE surface is low, wetting is difficult using only water, which has a high surface energy (~71.50 mN/m). In the presence of surfactant solution, the surfactant molecules adsorb on the PTFE surface and make it hydrophilic by increasing the surface energy. In this process, knowledge of the change in wetting free energy is also very important; larger values of the negative wetting free energy are expected to enhance the wetting process. From the thermodynamic point of view, the molar wetting free energy of the solid can be calculated according to Extrand[37] as

$$\Delta G = \frac{RT}{3} \ln \frac{(1 - \cos\theta)^2(2 + \cos\theta)}{4} \qquad (15)$$

Figure 9 shows that, with the increase in surfactant concentration, the wetting free energy becomes more negative and ultimately reaches a constant value above the CMC.

3.10. Polar and Dispersion Forces of Surfactant Solutions. According to Fowkes,[38] the interfacial tension is the contribution of polar and dispersion forces. The air−water interfacial tension or surface tension can be written as

$$\gamma_{\mathrm{LG}} = \gamma_{\mathrm{L}}^{\mathrm{p}} + \gamma_{\mathrm{L}}^{\mathrm{d}} \qquad (16)$$

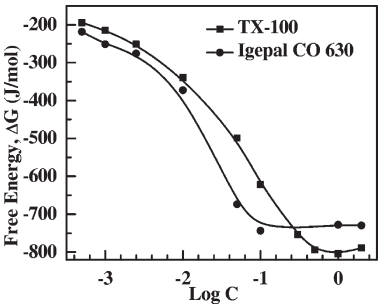

Figure 9. Change in the surface wetting free energy (ΔG) with concentration (log C) for different surfactants.

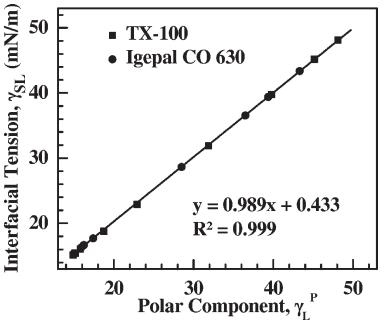

Figure 10. Plot of PTFE−water interfacial tension as a function of the polar component of the surface tension for different surfactants.

where $\gamma_{\mathrm{L}}^{\mathrm{d}}$ is the contribution of the dispersive forces and $\gamma_{\mathrm{L}}^{\mathrm{p}}$ is the contribution of the polar interaction term (mostly hydrogen bonding). Specifically, at the PTFE−water interface, the interfacial tension can be defined as the geometric mean of the dispersive force components

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SG}} + \gamma_{\mathrm{LG}} - 2\sqrt{\gamma_{\mathrm{L}}^{\mathrm{d}}\gamma_{\mathrm{S}}^{\mathrm{d}}} \qquad (17)$$

where $\gamma_{\mathrm{S}}^{\mathrm{d}}$ is the contribution of the dispersive forces of PTFE.

Rearranging the equation, one obtains

$$W_{\mathrm{a}} = 2\sqrt{\gamma_{\mathrm{L}}^{\mathrm{d}}\gamma_{\mathrm{S}}^{\mathrm{d}}} \qquad (18)$$

At the PTFE−air interface, an equation similar to eq 16 can be written by neglecting the polar component of surface tension, $\gamma_{\mathrm{SG}} = \gamma_{\mathrm{S}}^{\mathrm{d}} = 20.24$ mN/m.[5] Because the work of adhesion and γ_{LG} values are known for each surfactant concentration, the $\gamma_{\mathrm{L}}^{\mathrm{d}}$ value can be obtained from eq 16, and substituting the value into eq 16, one can calculate $\gamma_{\mathrm{L}}^{\mathrm{p}}$. The plot of $\gamma_{\mathrm{L}}^{\mathrm{p}}$ versus γ_{SL} for both surfactants (Figure 10) exhibits a linear relationship: $\gamma_{\mathrm{SL}} = 0.989\gamma_{\mathrm{L}}^{\mathrm{p}} + 0.433$. The direct determination of PTFE−water interfacial tension is difficult experimentally. However, there is good linear relationship between the polar component of the liquid and the solid−liquid interface, so γ_{SL} can be calculated from the polar component of the solution. It has also been observed that the relationship is independent of the type of surfactant; certain value of γ_{SL} can be obtained by maintaining a particular polar component of the liquid.

4. CONCLUSIONS

The adsorption kinetics and isotherms of TX-100 and Igepal CO-630 were found to follow pseudo-second-order kinetics and

the Langmuir isotherm model, with a higher adsorption constant rate constant and a higher Langmuir constant for Igepal CO-630.

The decrease in contact angle with increasing surfactant concentration follows a trend similar to that of the adsorption isotherm of the respective surfactant. The free energy of wetting becomes more negative with increasing surfactant concentration, indicating that the process is spontaneous for both surfactants. The Hamaker constant and work of adhesion decrease gradually with increasing surfactant concentration and ultimately reach plateau regions above the CMC. Igepal CO-630 shows a lower work of adhesion and Hamaker constant than TX-100. The change in the polar component of the interaction term with the PTFE−water interfacial tension follows the same linear relationship for both surfactants, so the PTFE−water interfacial tension is independent of the type of surfactant.

Igepal CO-630 has a lower CMC value and better wetting properties at low concentration than TX-100, as well as comparable properties near the CMC. As a result, the use of Igepal CO-630 as a wetting agent might be more beneficial than the use of TX-100 because of lower consumption in the process and possibly higher biodegradability in nature (because of the presence of a straight-chain hydrocarbon tail).

■ ASSOCIATED CONTENT

Supporting Information. Plots of surface tension (mN/m) versus adhesional tension (mN/m) and cos θ versus inverse surface tension for different surfactants. This material is available free of charge via the Internet at http://pubs.acs.org.

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Wetting of PTFE and Glass Surfaces by Aqueous Solutions of Cationic and Anionic Double-Chain Surfactants

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ABSTRACT: The wetting of hydrophobic and hydrophilic solid surfaces by surfactant solutions is an important research topic recently because of its profound practical applications. The wettability of two double-chain surfactants (cationic, didodecyldimethylammonium bromide or DDAB, and anionic, aerosol OT or AOT) solutions on poly(tetrafluoroethylene) (PTFE) and glass surfaces has been investigated here. Different physicochemical parameters such as critical micelle concentration (CMC) and surface tension, contact angle, surface excess at air−water and solid-water interfaces, work of adhesion, and free energy of wetting have been estimated for two double-chain surfactants solutions and compared with the reported results of single-chain surfactants. The double-chain surfactant solutions showed maximum lowering of surface tension values (24.36 and 26.35 mN/m for DDAB and AOT, respectively) and a change in contact angle values from pure water on PTFE (∼38° for DDAB and AOT) and glass (∼26.5 and 24° for DDAB and AOT, respectively) surfaces compared to the conventionally studied single-chain surfactants. The surfactant molecules mostly formed a monolayer adsorption on both surfaces during the wetting process. The surface excess values of both of the surfactants on PTFE−water and glass−water interfaces are 0.759 and 0.850 times lower than that of the air−water interface, respectively.

1. INTRODUCTION

Wetting of solid surfaces by surfactant solutions is important for many applications. The reported studies show there have been extensive studies on wetting of low-energy (hydrophobic) solid surfaces[1,2] compared to high-energy (hydrophilic) solid surfaces[3,4] using different surfactants. Surfactant solutions play an important role in the wetting process by changing water surface tension and solid−water interfacial tension because of adsorption of surfactant molecules at the interfaces. Most of the wettability studies on solid surfaces are focused on aqueous solutions of different single-chain surfactants,[2,4] the effect of different additives,[5,6] and mixed surfactants[7,8] but are rare on double-chain surfactants.[9,10] Double-chain surfactants are generally of two hydrocarbon chains on a headgroup or dimeric with two head groups (Gemini). Double-chained surfactants have continued to have more and more scientific interest over the past one or two decades because of their superiority over the single-chain surfactants.

The reported studies show Gemini surfactants have many superior features such as good water solubility, low critical micelle concentration (CMC), low Krafft point (at this temperature the solubility of the surfactant is equal to the CMC, below which the surfactant remains in crystalline form), and excellent surface activity in aqueous solution compared to conventional single-chain surfactants due to their unique structures.[11] Additionally, the nature of the spacer group is also most important in determining the solution properties of Gemini surfactants. Reported data on solution behavior of different Gemini surfactants show although they have low CMC values of 0.00591−0.093 mM,[12−16] only a few have a low minimum surface tension value (≤25 mN/m) at CMC compared to conventional single-chain surfactants.[12,15] Similarly double-chain surfactants also show superior surface activity compared to conventional single-chain surfactants because of similar reasons mentioned before. However, most of the double-chain surfactants show a comparatively lower minimum surface tension value than the Gemini surfactants.[17,18]

There are several studies available on the wettability of single-chain surfactants on hydrophilic and hydrophobic surfaces but a limited number on Gemini[9,19−21] or double-chain surfactants.[10,22−25] Seredyuk et al.[19] have studied the wettability of a zwitterionic Gemini surfactant of dissimilar chain lengths on a porous paper surface. Cao et al.[9] studied the wettability of cationic Gemini surfactant $[C_{12}-C_6-C_{12}]Br_2$ on silica surface and showed initially there was an increase in contact angle (51−63°) with the increase in surfactant concentration, which then again decreased to 31° because of formation of surface aggregation by the surfactant molecules. A similar observation was also found using imidazolium Gemini surfactant ($[C_{12}-C_4-C_{12}im]Br_2$) on the silicon wafer surface with a minimum contact angle of ∼41°.[21] They also reported the contact angle decreases until the concentration of 5 CMC because of the formation of multilayer adsorption.

The wettability of anionic double-chain surfactant aerosol OT (AOT) was studied on both the low surface energy hydrophobic (PTFE and PMMA) and hydrophilic (glass) surfaces.[1,20,22] Harkot and Janczuk[10,22] found the surfactant formed a monolayer adsorption on the solid−water interface and adsorption density at air−water and PTFE−water interfaces were equal. However, the adsorption densities at PMMA−water and glass−water interfaces were different from that of the air−water interface. Wettability on powder surfaces (alumina, silica) was also reported using double-chain

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surfactants.[24,25] Bi et al.[25] synthesized a double-chain surfactant, *N*,*N*-dipalmitoylethylenediaminediacetic acid sodium salt ($Di_{16}EDDA$), and it was found to have very good wetting property on silica powder compared to AOT.

In this paper we report on the wetting of PTFE and glass surfaces using aqueous solutions of cationic (DDAB) and anionic (AOT) double-chain surfactants. The novelty of this work is that wettability of anionic and cationic two double-chain surfactants on hydrophobic and hydrophilic surfactants is studied, and the values are compared with the reported studies of different single-chain surfactants. The study shows the use of cationic double-chain surfactant would be more effective for wetting of the PTFE surface than the conventional single-chain surfactants, which in turn may indirectly reduce the environmental problem as well as the process cost.

2. EXPERIMENTAL SECTION

2.1. Materials. A poly(tetrafluoroethylene) (PTFE) slide of dimensions 25.34 mm ×1.12 mm was cut from a sheet purchased from J. Khushal Das and Co., Mumbai, India, and the microscopic glass slides of 25.02 mm × 1.26 mm were purchased from Blue Star, India. The double chain surfactants, didodecyldimethylammonium bromide (DDAB) and aerosol OT (AOT), were purchased from Sigma–Aldrich Chemicals, Münich, Germany (catalog nos. 93418 and 542334, respectively) and used without any further purification. The structures of the surfactants used in this study are presented in Figure 1. Ultrapure water of 18.20 MΩ·cm resistivity, ~71.50 mN/m surface tension, and 6.5–7.0 pH was used for all of the experiments.

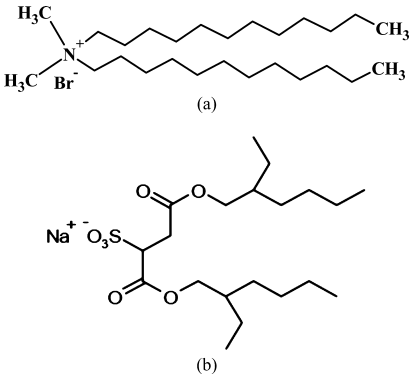

Figure 1. Structure of double-chain surfactants: (a) DDAB and (b) AOT.

2.2. Measurement of Surface Tension and CMC. All of the surfactant solutions were prepared freshly just before the measurements. The surface tension of aqueous surfactant solutions were measured by the Wilhelmy plate method using a surface tensiometer (Data Physics, Bad Vilbel, Germany, DCAT-11EC) at 25 ± 0.5 °C; the constant temperature was maintained using an external water circulator. The motor speed was 1 mm/s, and immersion depth of the platinum plate in the surfactant solution maintained was 3 mm. After measurement of each concentration the plate was cleaned with water and acetone and finally burned in alcohol flame. The CMCs of DDAB and AOT were found to be 0.05 and 0.2 mM, respectively, obtained from the surface tension data by the Wilhelmy plate technique.

2.3. Measurement of Contact Angle. Dynamic advancing (θ) contact angle was measured by Wilhelmy balance technique using the surface tensiometer at constant temperature (25 ± 0.5 °C). The motor speed of 1 mm/s and immersion depth of 5 mm were maintained during the contact angle measurements. Good quality PTFE and glass plates were chosen and washed several times with first acetone and then ultrapure water to clean the impurity. The plates were then dried by blowing hot air. The same procedure was repeated after the measurement of each surfactant concentration. The measurements were repeated thrice, and the average values are reported.

2.4. FT-IR Spectroscopy. Infrared spectroscopy was done using a Fourier transform infrared (FT-IR) spectrophotometer (IRPrestige-21, Shimadzu, Kyoto, Japan) in transmission mode, after the adsorption of DDAB on PTFE and glass slides. Adsorption was done from 1 mM DDAB solution for 3 h equilibrium time, and then the slides were dried at 50 °C to remove water. The spectra were taken at 4 cm^{-1} resolution. Background spectra were taken using bare PTFE and glass slides.

3. RESULTS AND DISCUSSION

3.1. Surfactant Adsorption at Air–Water Interface. The adsorption efficiency of surfactant molecules at the air–water interface is generally considered as an indicator of surface activity of a surfactant. The surface tension values of the double-chain cationic and anionic surfactant solutions versus logarithm of concentrations are presented in Figure 2. The

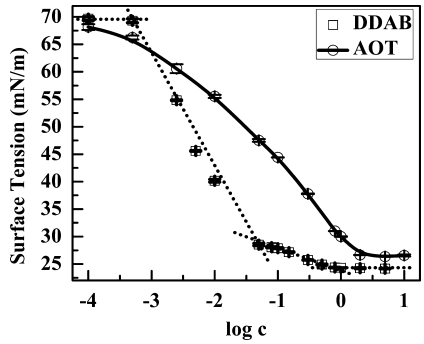

Figure 2. Change in surface tension (mN/m) with the concentration (log *c*) of different surfactants.

figure depicts the solution behavior with the increasing concentrations are different for two double-chain surfactants studied here. AOT shows there is a gradual decrease in surface tension until the CMC; beyond that concentration surface tension values are almost constant, similar to the conventional single-chain surfactants. In contrast, DDAB shows two transition points. Initially there is a sharp decrease in surface tension and then a change of slope at 0.05 mM (log $c = -1.3$); further at 0.8 mM (log $c = -0.09$) a second break of slope is observed. The first break is because of the formation of the micelle in the solution, and the second break point of the surface tension corresponds to the transition from micelles to small unilamellar or large multilamellar vesicles, referred to as a critical vesicle concentration (CVC).[18] The slopes of the linear portion of log *c* vs surface tension plot of two different regions are −20.77 and −3.91 for DDAB, indicating the slope in the micellization region is much greater than the region for vesicle

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formation. While comparing the slopes of the first region for two surfactants, it is observed that DDAB has a much higher slope than AOT (−9.83). The minimum surface tension value obtained for DDAB was also lower (24.36 mN/m) than AOT (26.351 mN/m); at the same time DDAB was also having much lower CMC (0.05 mM) than AOT (2 mM). On the other hand, these surface tension values are also significantly lower than the conventional single-chain cationic (CTAB = 32.99 mN/m), anionic (SDBS = 34.22 mN/m),[5] and nonionic (TX-100 = 31.01 mN/m, Igepal CO-630 = 31.02 mN/m)[2] surfactants frequently used for several applications. Since lowering of surface tension to a lesser extent is an important criterion to show the better surface activity of any surfactant, these surfactants are expected to have better interfacial properties. The area occupied per molecule for DDAB and AOT was calculated using Gibbs adsorption equation from the surface tension data below the first break point region. The values obtained are 91 and 192 Å^2/molecule for DDAB and AOT, respectively. Lower area per molecule also indicates the closer packing of DDAB molecules at the air−water interface.

3.2. Wetting of DDAB and AOT on PTFE and Glass Surfaces. The changes in advancing contact angle values with the increasing concentration (log c) of DDAB and AOT are presented in parts a and b of Figure 3, respectively, for PTFE and glass surfaces. Figure 3a clearly shows the dependency of contact angle with the logarithm of concentrations on the PTFE surface, which is similar to that of the surface tension for both surfactants. For the DDAB surfactant first and second slopes are −16.85 and −3.30, respectively, whereas for AOT it is −9.00. The minimum contact angle values obtained were 79 and 78.5° for DDAB and AOT, respectively, compared to 116.5° for pure water. So the total decrease in contact angle is ∼38° with respect to pure water for both surfactants. The contact angle in the presence of DDAB is 83° at CMC, and above that concentration at CVC the value reduces to 79°. The limiting contact angle values are very close for both surfactants, but the final concentration is 2.5 times lower for DDAB (0.8 mM) than AOT (2 mM). It can also be observed that the final contact angle values for both double-chain surfactants are significantly lower than the commonly used cationic (CTAB = 84.06°), anionic (SDBS = 86.76°),[5] and nonionic (TX-100 = 81.08°, Igepal CO-630 = 83.33°) surfactants.[2] The gradual decrease in the contact angle values are similar to that of the change in surface tensions, indicating probably DDAB and AOT molecules are adsorbed as a monolayer on the PTFE surface; the formation monolayer adsorption of DDAB on PTFE surface was also reported before.[26] If the consumption surfactants are calculated for wetting with reference to the concentration where plateau level contact is achieved, it can be found that the DDAB consumption is 60% lower than AOT and similar to CTAB but the minimum contact angle is 5° lower than CTAB. However, if the comparison is made at a particular contact angle of 84° (minimum achieved by CTAB), then the consumption of DDAB is 93% lower.

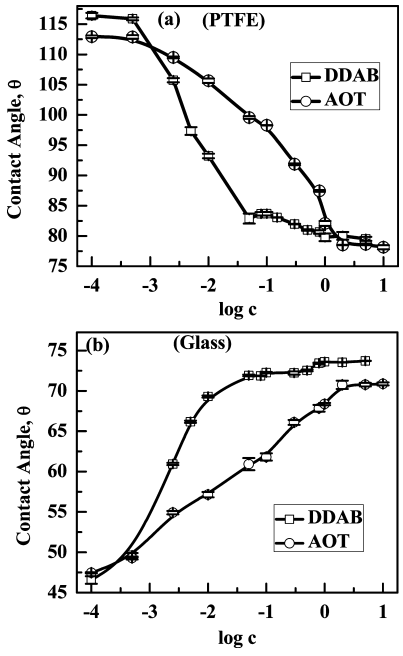

Figure 3. Change in contact angle (θ) with the concentration (log c) of different surfactants on (a) PTFE and (b) glass surfaces.

In the case of the hydrophilic glass surface AOT shows there is a linear increase in contact angle with the increase in the logarithm of the surfactant concentration, and when the concentration is above 2 mM, the contact angle reaches to a plateau level (Figure 3b). The change in contact angle is 46.5° (pure water) to 70.7°. In the presence DDAB initially there is a rapid increase in contact angle until the concentration of 0.01 mM, above that concentration the rate of increase is slower; finally above 0.8 mM concentration the contact angle reaches a steady value of 73°. Both surfactants show slightly higher contact angle values than the conventional different single-chain surfactants such as cationic (CTAB = 62.5°), anionic (SDBS = 59.33°), and nonionic (TX-100 = 68.8°, Igepal CO630 = 68.68°). From Figure 3b it can be observed that the adsorption of surfactant makes the hydrophobic PTFE surface to hydrophilic and exactly reverse for the hydrophilic glass surface. Previously reported contact angle studies using single-chain cationic surfactants on a glass surface showed initially there was an increase in contact angle and then again a decrease with the increase in surfactant concentration because of the formation of an adsorbed bilayer on the surface.[4] However, the present study shows no decreasing trend in the contact angle at higher surfactant concentration, indicating the probable monolayer adsorption of DDAB on the glass surface; as a result there is a gradual increase in hydrophobicity. The monolayer formation of DDAB is also consistent with the findings of Lu et al.[27] for adsorption of DDAB at the silica surface. They have reported the formation of surfactant monolayer on the silica surface, and the molecular parking area was ∼0.9 times of monolayer in the saturation level obtained from the air−liquid interface. In the present study the lower saturation level (0.84 times, discussed in section 3.4) on the glass surface can be attributed to a lower surface area of the flat surface compared to small particles reported before,[27] less contact time (∼25 s) between the solid surface and surfactant solution during the dynamic contact angle measurement. The schematic diagram of the adsorption layers on glass and PTFE surfaces using double-chain surfactants is shown in Figure 4.

3.3. Characterization of Surfactant Adsorption on PTFE and Glass Surfaces by FTIR. To get some qualitative idea about the arrangement of the adsorbed surfactant molecules on PTFE and glass surfaces in terms of molecular interaction, FT-IR analysis was done for DDAB. Because the methylene (-CH_2) vibration is sensitive to the molecular interaction of the hydrophobic chains, the peak position of the

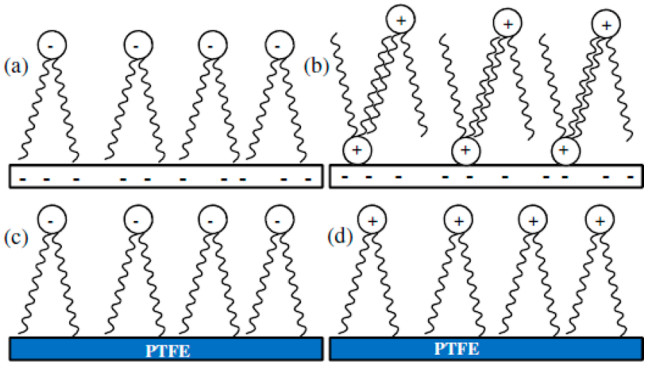

Figure 4. Schematic diagram of the adsorption layer of double chain surfactants: (a) AOT on the glass, (b) DDAB on the glass, (c) AOT on the PTFE, and (d) DDAB on the PTFE surfaces.

methylene stretching can be used to get an idea about the adsorption pattern of the surfactant molecules on the solid surface. Figure 5 shows the FT-IR spectra of surfactant

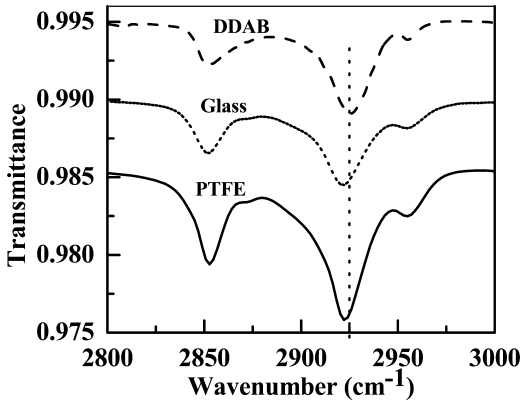

Figure 5. FTIR spectra of DDAB on PTFE and glass surfaces.

molecules on the PTFE surface after dipping in 1 mM DDAB solution for 3 h equilibrium time. For pure DDAB surfactant the -CH_2 asymmetric (ν_{as}) and symmetric (ν_s) vibration bands were obtained at ~2926 and ~2855 cm^{-1}, respectively. These values are close to those of reported values of 2926 and 2853 cm^{-1} respectively for octadecyltrimethylammonium bromide (C_{18}TAB) surfactant.[28,29] After adsorption of surfactant on PTFE surfaces it was found that the ν_{as} and ν_s vibration bands shifted toward lower wavenumber, obtained at ~2922 and ~2852 cm^{-1}, respectively. A 4 cm^{-1} shift in ν_{as} vibration band toward lower wavenumber may be attributed to tail−tail interaction between the surfactant molecules because of the close-packed adsorption of molecules on the PTFE surface, which in turn reduced the freedom of the surfactant molecules as well as stretching vibrations. After adsorption of surfactant on the glass surface it was found that the ν_{as} and ν_s vibration bands of the methylene (-CH_2) group were obtained at ~2922 and ~2852 cm^{-1}, similar to that of the PTFE surface. On the glass surface, although the adsorption pattern is reverse, the shift in vibration bands may be because of a similar tail−tail interaction of surfactant molecules as suggested schematically in Figure 4.

3.4. PTFE−Water and Glass−Water Interfacial Tension. Adsorption of surfactant at air−water and solid−water interfaces changes the surface or interfacial tensions at the respective interfaces, which is again closely related to wetting of a solid surface. The contact angle can be related to the surface or interfacial tensions using Young's equation as

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos\theta \quad (1)$$

To get a relationship between the contact angle and surface excess at the interfaces, Young's and Gibbs equations can be combined as follows[30,31]

$$\frac{d(\gamma_{LG} \cos\theta)}{d(\gamma_{SG})} = \frac{\Gamma_{SG} - \Gamma_{SG}}{\Gamma_{LG}} \quad (2)$$

For the present study Γ_{SG}, Γ_{SL}, and Γ_{LG} represent the surface excess of surfactants at the PTFE−air, PTFE−water, and air−water interfaces, respectively.

If the surface excess at the solid−air interface is assumed to be zero ($\Gamma_{SG} = 0$, because there is no contact with the solution), the ratio of surface excess at the soild−water and air−water interfaces (Γ_{SL}/Γ_{LG}) can be obtained from the slope of γ_{LG} cos θ or adhesion tension versus γ_{LG} plot. The surface excess values of surfactants at the solid−water and air−water interfaces are dependent on the slope of the linear relationship; such as $\Gamma_{SL} = \Gamma_{LG}$ (slope = 1), $\Gamma_{SL} > \Gamma_{LG}$ (slope > 1), and $\Gamma_{SL} < \Gamma_{LG}$ (slope < 1). The plots of adhesion tension versus surface tension for DDAB and AOT show there are linear relationships on both the PTFE and glass surfaces (Figure 6). The average slopes on

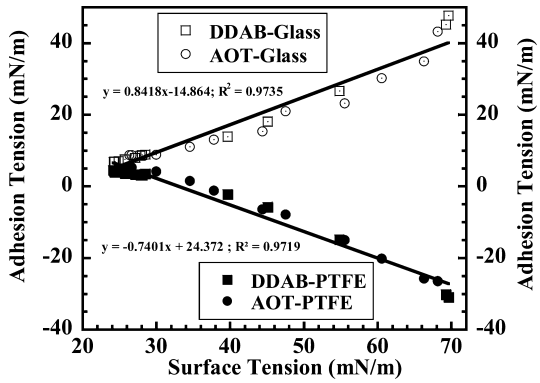

Figure 6. Plot of surface tension (mN/m) vs adhesion tension (mN/m) of DDAB and AOT on PTFE and glass surfaces.

PTFE and glass surfaces are −0.759 (DDAB = −0.745, AOT = −0.775) and +0.840 (DDAB = 0.831, AOT = 0.854), respectively. These results qualitatively demonstrate that the surface excesses at both the solid−water interfaces are less than that at the air−water interface for both the double-chain surfactants. The unequal surface excesses at PTFE−water and air−water interfaces were also reported before for the single-chain surfactants.[2,6] However, while comparing the slopes obtained from the present to our previous studies, it can be concluded that these double-chain surfactants are having less surface excess at the solid−water interface than the air−water interface. The reported values of the $\Gamma_{PTFE-water}/\Gamma_{air-water}$ ratio using different single-chain surfactants, such as Igepal CO-630, TX-100, CTAB, and SDBS are in the range of 0.83−0.86.[2,6] This fact can be attributed to the adsorption pattern of surfactant molecules on the PTFE surface. At the air−water interface double-chain surfactant molecules are giving a better close packing structure, keeping the tailgroup outward direction because of greater hydrophobic interaction between the tailgroups of the surfactant molecules. However, at the PTFE−water interface double-chain surfactant, molecules

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adsorbed with less flexibility compared to single-chain molecules, which mostly make a monolayer, as a result, lowers molecular density.

The results of the glass−water interface show the linear relationship between the adhesion tensions versus surface tension with an average slope of 0.84, indicating unequal adsorption at glass−water and air−water interfaces. The studies on single-chain surfactants showed the slope was different for each individual surfactant; the cationic surfactant also showed higher adsorption density at the solid−water interface ($\Gamma_{SL}/\Gamma_{LG} > 1$), attributed to the formation of multilayer adsorption.[32] In contrast, for both the cationic and anionic double-chain surfactants, the surface excess at the glass−water interface is a little higher than the PTFE−water interface, but still less than that of air−water interface, maybe because of the monolayer adsorption as discussed before.

Figure 6 clearly shows there is a crossover point between the adhesion tensions on PTFE and glass surfaces. The crossover point is at 25 mN/m surface tension and 5 mN/m adhesion tension. Since the minimum surface tension of 25 mN/m is achieved by DDAB at CMC, so the crossover point occurs in the presence DDAB where both the surfaces are having the same adhesion tension. In contrast, our previous studies using nonionic surfactants (Igepal CO-630 and TX-100) showed there was no crossover point, as those surfactants could not reach to that much lower surface and adhesion tensions. This may be called as critical adhesion tension for the solid−water interfaces, where both the hydrophilic and hydrophobic surfaces are having equal adhesion tension and wetting toward a particular surfactant solution.

The area occupied per surfactant molecules at any interface can give some idea about the packing as well as the orientation pattern. The area occupied per molecule (A_{air}) of DDAB and AOT is found to be 91 and 192 Å^2, respectively, mentioned before. Since the surface excess of the surfactant at the PTFE−water interface is 0.75 times less than that of the air−water interface, hence, the areas per surfactant molecules at the PTFE−water interface are 121.33 and 256 Å^2 for DDAB and AOT, respectively. Similarly, because the surface excess of surfactants at the glass−water interface is 0.84 times lower than that of air−water interface, the values of A_{glass} obtained are 108 and 229 Å^2 for DDAB and AOT, respectively. The molecular density results indicate double-chain surfactant solutions are able to change the contact angle on hydrophilic and hydrophobic surfaces to a greater extent than the single-chain surfactants although the area occupied per molecule is less for the former case.

3.5. Work of Adhesion of Surfactants Solutions. The work of adhesion of a liquid to solid, W_A, is defined by the reversible work required to separate a unit area of liquid from a solid surface and can be calculated by using the following equation

$$W_A = \gamma_{LG} + \gamma_{SG} - \gamma_{SL} \quad (3)$$

Introducing the Young equation,

$$W_A = \gamma_{LG}(\cos\theta + 1) \quad (4)$$

The work of adhesion of surfactant solutions on PTFE and glass surfaces was calculated by putting the contact angle and surface tension values in eq 4 and presented in Figure 7.

From the figure it can be observed that the work of adhesion (W_A) decreases with the increasing concentration of surfactants (DDAB and AOT) on both PTFE and glass surfaces. While

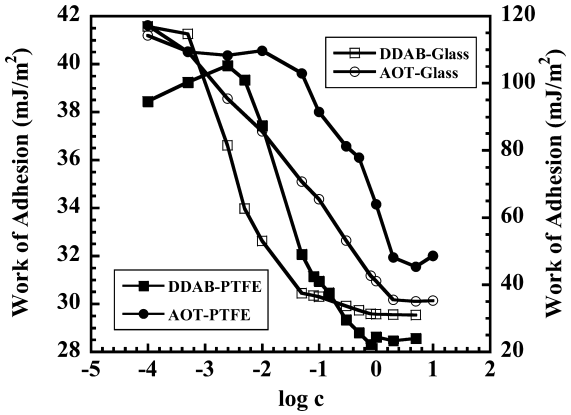

Figure 7. Change in work of adhesion (W_A) with the concentration (log c) of different surfactants.

comparing the adhesion tensions of DDAB and AOT on the PTFE surface, it can be found that adhesion tension in the presence of DDAB is lower than AOT. In contrast, on the glass surface, DDAB shows lower adhesion tension below the CMC region, but the difference is not very significant above the CMC region. The work of adhesion of pure water for PTFE and glass surfaces is 39.59 and 120.71 mJ/m^2, respectively. The work of adhesion of DDAB solutions on PTFE and glass surfaces above the CMC is 28.55 and 30.94 mJ/m^2, respectively, whereas that of AOT solutions on PTFE and glass surfaces is 32 and 35.24 mJ/m^2, respectively, above the CMC.

3.6. Wetting Free Energy on PTFE and Glass Surfaces. The surface free energy quantifies the strength of interaction of the spread liquid onto the solid surface. From the thermodynamic point of view the molar wetting free energy of the solid can be calculated using eq 5 according to Extrand.[33]

$$\Delta G = \frac{RT}{3}\ln\left(\frac{(1-\cos\theta)^2(2+\cos\theta)}{4}\right) \quad (5)$$

where ΔG is the surface free energy, R is (8.314 J mol^{-1} K^{-1}) the universal gas constant, and T is temperature in kelvin. The free energies of wetting on the PTFE surface are more negative ($\Delta G_{PTFE-DDAB}$ = −831.73 J/mol; ($\Delta G_{PTFE-AOT}$ = −871.66 J/mol) in the presence of surfactant solutions above the CMC than pure water (−171.54 J/mol). However, on the glass surface the free energies of wetting are less negative ($\Delta G_{glass-DDAB}$ = −1007.63 J/mol; $\Delta G_{PTFE-AOT}$ = −1102.97 J/mol) than pure water (−2253.88 J/mol). But the surface free energies of glass for both the surfactants are more negative compared to the PTFE surface.

4. CONCLUSIONS

Double-chain cationic (DDAB) and anionic (AOT) surfactants show a lower value of minimum surface tension at the CMC compared to that of commonly used single-chain surfactants. The plot of surface tension vs concentration of DDAB shows two break points in slope because of the formation of micelle first and then vesicle, with higher slope at the micellar region. The surfactant concentration to achieve plateau level surface tension and the minimum surface tension values are lower for DDAB than AOT; subsequently adsorption density of DDAB is higher at the air−water interface than AOT. The wetting of the PTFE surface in the presence of both the double-chain surfactants are similar in terms of a decrease in contact angle

and much better than the conventional single-chain surfactants; however, the final concentration required for DDAB is lower than AOT. In the case of the glass surface the increase in contact angle is slightly more for DDAB. There is a linear relationship of adhesion tension and surface tension with slopes of −0.759 and +0.840 on PTFE and glass surfaces, respectively, for both surfactants; the slope values below one indicate surface excess of surfactant molecules at the solid−water interfaces are less than that of the air−water interface. DDAB solutions show a critical adhesion tension for the PTFE−water and glass−water interfaces, where both the hydrophilic and hydrophobic surfaces are having equal adhesion tension and wettability. The free energies of wetting on the PTFE surface are more negative in the presence of surfactant solutions than pure water. However, on the glass surface the free energies of wetting are less than pure water but free energies of wetting on the glass surface are still more negative than PTFE for both surfactants. Finally, it can be concluded that the double-chain cationic and anionic surfactants are having better wettability on the PTFE surface compared to single-chain surfactants. The use of cationic double-chain surfactant (DDAB) may reduce the consumption of surfactant to a value of 93 and 60%, respectively, compared to that of CTAB and AOT for wetting of the PTFE surface.

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Notes

The authors declare no competing financial interest.

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